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(DOKLADY AKADEMII NAUK SSSR)

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Volume 2

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Edited by C. W. Sanders
Engineering Department, E. I. du Pont Company
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CONDENSATION OF TETRAALKYLSILANES IN A HIGH-VOLTAGE, SONIC-FREQUENCY SILENT DISCHARGE

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Up to the present time, no one has studied the effect of electrical discharges on tetraalkylsilanes. It is known that saturated hydrocarbons will condense to liquid products under the influence of silent discharges [1], the product consisting of a mixture of saturated and unsaturated polymers.

On the basis of the results of previous investigations of the effect of silent discharges on different organosilicon compounds [2-4], it would be expected that tetraalkylsilanes would also condense with the formation of polymeric compounds containing alternating Si and C atoms in the main chain. Trimethylethyl-and dimethyldiethylsilanes were selected for study in the present investigation. There are four different types of bonds in both of these silicon-containing hydrocarbons: $Si-CH_3$ (74-76 kcal/mole) [5], $Si-C_2H_5$ (59-64 kcal/mole) [5], C–C (80-85 kcal/mole), and C–H (94-97 kcal/mole). The bond energy values cited for the last two types of bonds are those calculated for hydrocarbons [6]. An investigation of the composition and structures of the condensation products should yield additional information on the degree of stability of the different types of bonds under the action of such discharges.

The experimental method was similar to that used in a similar investigation of hexamethyldisiloxane [4]. Vapors of the silane were mixed with H_2 and passed once through the silent discharge zone. The discharge potential was 6.5-6.8 kv and the frequency was 4000 cycles per second.

Ethylene and acetylene were identified among the gaseous reaction products obtained from trimethylethylsilane, and tetramethylsilane (I), hexamethyldisilane (II), 3,3,5,5-tetramethyl-3,5-disilahexane (III), and 3,3,4,5,5-pentamethyl-3,5-disilahexane (IV) were identified among the liquid products. In addition to these compounds, which have the composition $C_8H_{22}Si_2$ and $C_9H_{24}Si_2$, the presence in the high-boiling products of silicon-containing hydrocarbons having the composition $C_{12}H_{32}Si_3$ (V) was demonstrated; these constituted a difficulty separable mixture of isomers. The high-molecular-weight polymers boiling above 220°C (5 mm) (VI) had an average molecular weight of 1690 and corresponded to the composition $(C_{3,8}H_9Si)x$. Thus, the C/Si ratio of the condensation products was significantly lower than that of the original $(CH_3)_3SiC_2H_5$ and decreased monotonically from 5:1 to 3.8:1. It follows that this polycondensation process is not a simple dehydrocondensation (proceeding through rupture of C–H bonds), but is a more complex process which depends on rupture of $Si-CH_3$ or $Si-C_2H_5$ bonds. That C–C bonds do not rupture under the conditions employed was demonstrated by an experiment with normal hexane carried out under analogous conditions. Since this hydrocarbon did not undergo any change, it may be assumed that the C–C bond in the ethyl radical of the trimethylethylsilane is sufficiently stable that there is no appreciable bond rupture under the conditions of our experiments. The formation of small amounts of $(CH_3)_4Si$ could be due to dissociation of $\equiv SiCH_2-CH_3$ bonds, but it is more probable that this compound was formed by recombination of $\dot{C}H_3$ and $(CH_3)_3\dot{S}i$ radicals. The isolation of large amounts of (III) also confirms that the C–C bond is stable under the conditions of our experiments.

Dissociation of Si–C bonds may be considered to be the primary act under the influence of the discharge.

$$(CH_3)_3SiC_2H_5 \rightarrow (CH_3)_3\dot{S}i + \dot{C}_2H_5 \quad (1)$$

$$(CH_3)_3SiC_2H_5 \rightarrow C_2H_5(CH_3)_2\dot{S}i + \dot{C}H_3 \quad (2)$$

Further reactions of the methyl and ethyl radicals lead to the formation of C_2H_2, C_2H_4, and H^*. The absence in the condensate of compounds with an Si–Si bond suggests that recombination reactions among the organosilicon radicals (obtained by Reactions (1) and (2)) do not occur.

The formation of these free radicals and H atoms must lead to the occurrence of chain reactions [7]. That hydrocarbons subjected to the action of an electrical discharge can undergo chemical reactions by a chain mechanism has previously been demonstrated by A. A. Balandin, Ya. G. Éidus and N. G. Zalogin [8].

The H^* and CH_3 formed in the primary reactions can bring about the formation of secondary radicals; for example:

$$C_2H_5Si(CH_3)_3 + \dot{H}\ (\dot{C}H_3) \rightarrow \begin{cases} C_2H_5(CH_3)_2Si\dot{C}H_2 + H_2\ (CH_4) & (3) \\ (CH_3)_3SiCH_2\dot{C}H_2 + H_2\ (CH_4) & (4) \\ (CH_3)_3Si\dot{C}HCH_3 + H_2\ (CH_4) & (5) \end{cases}$$

Recombinations of these secondary radicals among themselves and with the primary radicals (formed by Reactions (1) and (2)) leads to the formation of the simplest condensation products with the compositions $C_8H_{22}Si_2$ and $C_9H_{24}Si_2$, for example, II, III, and IV.

The large amount of (IV) among these compounds is quite understandable, and it may be explained by the higher energy of C–H bonds at secondary carbon atoms than at primary carbon atoms [6]. Hence, it follows that Reaction (5) must predominate over Reactions (3) and (4).

Investigation of the composition of the condensate obtained from dimethyldiethylsilane was a still more complex problem owing to the possibility of the formation of a greater number of isomeric compounds in this case. Isolation of individual compounds from this condensate was not possible. However, investigations of individual fractions of the condensate led us to conclude that compounds of the compositions $C_{10}H_{26}Si_2$, $C_{11}H_{28}Si_2$, $C_{14}H_{34}Si_3$, and $C_{19}H_{48}Si_4$ were present. The high-boiling polymers had an average molecular weight of 1050 and corresponded to the composition $(C_{4.5}H_{11}Si)_x$.

The compounds present in this condensate were also characterized by a continuous decrease in the C/Si ratio from 6:1 for the original $(CH_3)_2Si(C_2H_5)_2$ to 4.5:1 for the high-molecular-weight polymers, which indicates that the mechanism of their formation is similar to that of the polycondensation of trimethylethylsilane. Thus, polycondensation under the influence of electrical discharges, as studied in the present work, makes possible the single-stage preparation of polymeric silicon-containing hydrocarbons with a main chain of alternating Si and C atoms in yields of up to 40% of the original tetraalkylsilane.

Experimental

The experiments with trimethylethyl- and dimethyldiethylsilane were carried out in a previously described apparatus [4] by the same method. The starting materials had the following characteristics: trimethylethylsilane, b. p. 62-63°; n^{20}_D 1.3805; d^{20}_4 0.6846; dimethyldiethylsilane, b. p. 96-97°; n^{20}_D 1.4004; d^{20}_4 0.7166. The silanes were fed at a rate of 8-10 ml per hour, and the hydrogen feed rate was approximately 2.5 liters per hour. The potential in the secondary circuit was 6.5-6.8 kv in the experiments with trimethylethylsilane and 4.8-5.2 kv in the experiments with dimethyldiethylsilane.

Experiments with trimethylethylsilane. A total of 700 g of $(CH_3)_3SiC_2H_5$ was charged. The unreacted silane was removed by distillation, and 285 g of condensation products was obtained; this amounted to a yield of 41% based on the trimethylethylsilane charged. The effluent gas contained small amounts of acetylene and ethylene and, in addition, about 3 g of tetramethylsilane (I), b. p. 23-26°, n^{20}_D 1.3575; d^{20}_4 0.420. Literature values [9]:

b. p. 26°, n^{20}_D 1.3578; d^{20}_4 0.6411. The liquid condensation product was a yellowish, transparent, mobile liquid. According to the distillation data, the condensate contained 28-30% compounds containing two Si atoms per molecule, about 25% compounds with three Si atoms, about 10% with four Si atoms, and 30-35% high-boiling polymers containing more than four Si atoms in the molecule.

The following individual compounds were isolated from the condensate by fractional distillation:

Hexamethyldisilylethane (II) $(CH_3)_3Si-CH_2-CH_2-Si(CH_3)_3$. B.p. 26°/5 mm, 151-152°/760.8 mm; n^{20}_D 1.4200; d^{20}_4 0.7514, weight, 3.7 g.

Literature values [10]: b. p. 150-151°, n^{20}_D 1.4204; d^{20}_4 0.7536.

3,3,5,5-Tetramethyl-3,5-disilahexane (III) $C_2H_5(CH_3)_2SiCH_2Si(CH_3)_3$. B. p. 34-36°/5 mm; n^{20}_D 1.4266; d^{20}_4 0.7704; mol. wt. 168; calculated, 174.4. MR_D: found, 58.07; calculated, 58.43.

Found %: C 55.53; Si 32.21; H 12.23
$C_8H_{22}Si_2$. Calculated %: C 55.08; Si 32.21; H 12.71

Literature values [11]: b. p., 157-159°; n^{20}_D 1.4272; d^{20}_4 0.7713.

3,3,4,5,5-Pentamethyl-3,5-disilahexane (IV) $C_2H_5(CH_3)_2Si-\underset{\underset{CH_3}{|}}{CH}-Si(CH_3)_3$.

B. p. 63-65°/4 mm; n^{20}_D 1.4410; d^{20}_4 0.7900; mol. wt.: found, 203; calculated, 188.4. MR_D: found, 63.08; calculated, 63.06.

Found %: C 57.69; Si 29.14; H 12.70
$C_9H_{24}Si_2$. Calculated %: C 57.36; Si 28.81; H 12.84

Literature values [12]: b. p. 60°/10 mm; n^{20}_D 1.4405; d^{20}_4 0.7905.

In addition, three other silicon-containing hydrocarbons were isolated: a) B. p. 53-55°/6 mm; n^{20}_D 1.4350; d^{20}_4 0.7798; and b) b. p. 65-67/6 mm; n^{20}_D 1.4381; d^{20}_4 0.7860; mol. wt. 187-192; MR_D, 62.90 and 63.07. These corresponded to the composition $C_9H_{24}Si_2$, and were isomers of unestablished structure. c) B. p., 99-102°/4 mm (V); n^{20}_D 1.4590; d^{20}_4 0.8235; mol. wt.: found 269; calculated, 260.6. MR_D, found 85.44; calculated for $C_{12}H_{32}Si_3$, 86.58.

Found %: C 55.72; Si 31.63; H 12.53
Calculated %: C 55.30; Si 32.33; H 12.37

The high-boiling polymers boiling above 220°/5 mm (VI); n^{20}_D 1.4993; d^{20}_4 0.9272, comprised a yellowish, transparent oil. The average molecular weight was 1690. The composition corresponded to the formula $(C_{3.8}H_9Si)x$.

Experiments with dimethyldiethylsilane $(CH_3)_2Si(C_2H_5)_2$. A total of 374 g of dimethyldiethylsilane was charged. The condensate was light yellow in color. The unreacted silane was removed by distillation, and 82 g of condensation products was obtained. The yield was 22% based on the dimethyldiethylsilane charged. Acetylene was found in the effluent gases.

We were unable to isolate individual compounds by fractional distillation. Fractions were separated in which the presence of polymeric silicon-containing hydrocarbons of the following compositions was established:

1. B. p., 80-85°/5 mm; $n^{20}D$ 1.4450, d^{20}_4 0.8019; mol. wt.: found, 202; calculated 202.5. MR_D: found 67.21; calculated 71.46.

Found %: C 59.66; Si 27.65; H 13.18
$C_{10}H_{26}Si_2$. Calculated %: C 59.30; Si 27.86; H 12.93

2. B. p., 95-100°/5 mm; n^{20}_D 1.4487; d^{20}_4 0.8122; mol. wt.: found, 228; calculated, 216. MR_D: found, 71.46; calculated, 72.32.

Found %: C 60.66; Si 25.69; H 12.87
$C_{11}H_{28}Si_2$. Calculated %: C 60.95; Si 25.95; H 13.04

3. B. p., 125-140°/5 mm; $n^{20}D$ 1.4620, d^{20}_4 0.8359; mol. wt.: found, 273; calculated, 276.5. MR_D: found, 94.4; calculated, 93.71.

Found %: C 58.51; Si 30.00; H 12.16
$C_{14}H_{34}Si_3$. Calculated %: C 58.63; Si 29.40; H 11.96

4. B. p., 165-180°/5 mm; $n^{20}D$ 1.4710; d^{20}_4 0.8559; mol. wt.: found, 348; calculated, 388. MR_D: found, 126.8; calculated, 128.6.

Found %: C 58.53; Si 28.75; H 12.40
$C_{19}H_{48}Si_4$. Calculated %: C 58.67; Si 28.89; H 12.44

High-boiling polymers boiling above 210° at 3 mm; $n^{20}D$ 1.5056; d^{20}_4 0.9357. This was a viscous oil of the composition $(C_{4.5}H_{11}Si)x$; mol. wt., 1050.

Found %: C 58.01; Si 30.27; H 11.84
$(C_{4.5}H_{11}Si)x$. Calculated %: C 57.97; Si 30.13; H 11.89

When any of the fractions of either condensate was cooled to −78°, it remained fluid, and no crystals were formed.

The analyses were carried out in the Analytical Group under the direction of Yu. N. Platonov.

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DEVIATION OF THE STEREOISOMERIC 1,4-DI-TERT-BUTYLCYCLOHEXANES FROM THE AUWERS-SKITA RULE

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In 1956, we showed that 1,4-diisopropylcyclohexanes do not follow the rule of Auwers-Skita; specifically, the lower-boiling isomer has the cis configuration in this case [1]. This was later confirmed by stereospecific synthesis [2]. During the course of the latter work, it was found that the dimethyl esters of the stereoisomeric cyclohexane-1,4-dicarboxylic acids also deviate from the rule of Auwers-Skita in a completely analogous manner. Eliel and Haber [3] recently observed that the boiling points of all six stereoisomeric methylcyclohexanols contradict the so-called conformation rule— the current and more accurate expression of the Auwers-Skita rule. Thus, the cis isomers of the 2- and 4-methylcyclohexanols were the lower-boiling isomers, while with the 3-methylcyclohexanols, the trans form was the lower boiling. The American authors attributed these deviations to the effect of hydrogen bonding. Such an explanation would not be applicable to the esters which we have investigated, and especially not to the hydrocarbons; it is quite possible that the cause of this phenomenon would be different for the different classes of compounds. Therefore, it appeared of interest to attempt to find new examples of such deviations among hydrocarbons, where there could be no complicating effect of hydrogen bonding, polar atoms or groups, etc.

It appeared to us that the 1,4-di-tert-butylcyclohexanes might provide such an example. As a matter of fact, Mekhtiev and co-workers [4] synthesized this hydrocarbon [4], and, while attempting to separate it into its stereoisomers, they found that the lower-boiling isomer was a liquid, while the residue from the distillation congealed in the distillation flask and had an m. p. of 57°. Although these authors assigned the trans configuration to the lower-boiling isomer on the basis of the Auwers-Skita rule, there is reason to doubt this assignment, since in the 1,4-disubstituted cyclohexane series the higher melting point is a characteristic of the trans form, and in this case the higher-boiling isomer also had the higher melting point. Therefore, we resolved to repeat the synthesis of the 1,4-di-tert-butylcyclohexanes and to clarify their relationship to the Auwers-Skita rule. These compounds were prepared by alkylating benzene with isobutyl alcohol and hydrogenation of the resulting p-di-tert-butylbenzene in the presence of Raney nickel. The lower-boiling isomer was then distilled in a column having an efficiency of 100 theoretical plates, and the residue was repeatedly recrystallized from alcohol until the melting poing did not change during successive crystallizations. The properties of the resulting stereoisomers are shown in Table 1. The constants of the lower-boiling form are close to those cited by Mekhtiev and co-workers [4], although our preparation obviously was appreciably purer. However, as may be seen from our results, the higher-boiling substance described by these authors was not an individual compound, but was a mixture of both forms and contained a significant amount of the lower-boiling isomer.

It was shown in recently published work [6] that all of the 1,4-dialkylcyclohexanes studied by the authors gave Raman spectra in which the cis isomer was characterized by the presence of an intense line at 630 cm^{-1};

no such line was present in the spectra of the trans isomers. On the basis of this observation, spectroscopic investigation of our 1,4-di-tert-butycyclohexanes* confirmed our assumed configurations of the stereoisomers. Specifically, the spectrum of the lower-boiling isomer showed a line at 629(26); consequently, the cis configuration must be assigned to this isomer. Thus, we actually have here a new violation of the rule of Auwers-Skita.

TABLE 1

Physical Properties of the Stereoisomeric 1,4-Di-tert-butylcyclohexanes

Preparation	Isomer	B.p.		M.p., °C	n_D^{20}	n_D^{90}	d_4^{20}	d_4^{90}	Cryoscopic constant per mole, °C	Degree of purity, %
		°C/mm	°C/760 mm							
Present work	Cis-	120,0/20	234,9 **	20,8	1,4580	1,4300	—	0,7852	0,0181	99,9
Mekhtiev et al. [4]	Lower-boiling	96/10	239—240	18,5	1,4568	—	0,8309	—	—	96***
Present work	Trans-	121,7—122°,2/20	236,9 **—237,5	88,5	—	1,4290	—	0,7844	0,0165	99,9
Mekhtiev et al. [4]	Higher-boiling	—	242—243	57	—	—	—	—	—	—

Until very recently, the literature on this subject has stated that deviations from this rule are observed only for entire series of compounds of the same structure (1,3-dialkylcyclopentanes and 1,3-dialkylcyclohexanes). Data have now been accumulated which indicate that even within the bounds of a single series, the rule of Auwers-Skita can be both obeyed and violated. In such cases, either only the boiling points may be inverted (1,4-diisopropylcyclohexanes, methylcyclohexanols), or some other constant may be inverted at the same time. As has been shown quite recently [7], 1-phenyl-2-cyclopropyl- and 1,2-diphenylcyclopropanes exhibit the latter type of violation. Among these hydrocarbons, not only does the cis form boil lower, but it also has the lower index of refraction and density.

As may be seen from the data of Table 1, the stereoisomeric 1,4-di-tert-butylcyclohexanes deviate from the rule of Auwers-Skita in a manner similar to the 1,4-diisopropylcyclohexanes.

Experimental

1,4-Di-tert-butylbenzene. Benzene was alkylated with isobutyl alcohol in the presence of concentrated H_2SO_4 [8]. The original alcohol had the following properties: b.p., 107.0-107.2°/739 mm; n_D^{20} 1.3960 d_4^{20} 0.8012. Reliable literature values are [9]: b. p., 107.98°/760 mm; n_D^{20} 1.3959; d_4^{20} 0.80196. A total of 400 g of 1,4-di-tert-butylbenzene was obtained from several syntheses; after two recrystallizations from ether, this material had a freezing point of 76.2° (the literature [10] reports an m. p. of 77.7°). The freezing curve of this hydrocarbon is shown in Fig. 1b.

Stereoisomeric 1,4-di-tert-butylcyclohexanes. A solution of 150 g of 1,4-di-tert-butylbenzene in 250 g of n-heptane was hydrogenated in an autoclave at an initial hydrogen pressure of 140 atm and a temperature of 190-200°. The Raney nickel catalyst was prepared as described previously [1]. At the conclusion of the hydrogenation, the solution was filtered from the catalyst and chromatographed twice on silica gel (174-180 g) for removal of the unreacted aromatic hydrocarbon. The heptane was then distilled, and the residue (108.8 g), which consisted of crystals and liquid, was filtered through a glass filter. The crystalline material (70.0 g) was distilled in a column having an efficiency of 100 theoretical plates. The distillation was carried out over a period of several days at high reflux ratios (150-200). In order to avoid crystallization of the distillate in the cold parts of the apparatus, hot water circulated through the condenser, and all exterior parts of the apparatus and column were wrapped with thin foil, through which an electric current was passed. During the distillation, 14 narrow fractions having volumes

* It was not possible to determine the boiling point accurately in view of the high melting point. The value presented was obtained during distillation from a Favorskii flask.

** Calculated by means of Dreisbach's tables [5].

*** Calculated by us on the basis of the cryoscopic constant presented above and a m.p. of 18.5°.

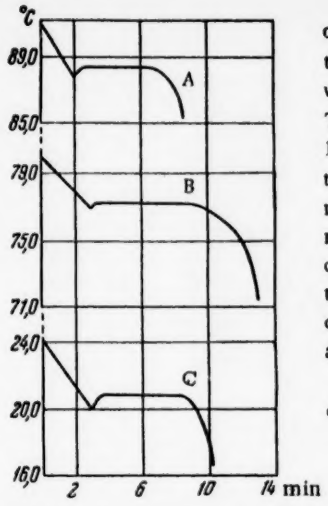

Fig. 1. Freezing curves of the hydrocarbons investigated. A) Trans-1,4-di-tert-butylcyclohexane, B) 1,4-di-tert-butylbenzene, C) cis-1,4-di-tert-butylcyclohexane.

of 1.5-5 ml were collected, and the freezing curve was determined for each of these fractions. Judging from these curves, the purest lower-boiling substance was contained in four of these fractions which had the same constants (shown in Table 1 as properties of the cis isomer); the freezing curve is presented in Fig. 1C. A total of 23.3 g* (33.3%) of the lower-boiling isomer was collected. A total of 6.8 g (9.7%) of intermediate fractions was collected; these fractions had melting points which gradually increased from 23.4 to 40°. The residue, which melted at 58-68°, amounted to 39.2 g (56.0%). It was subjected to repeated recrystallization. Separation of the isomers was difficult, and eight recrystallizations were required to isolate the pure high-boiling isomer (9.0 g). The freezing curve of this material is shown in Fig. 1A, and its constants are given in Table 1 as the properties of the trans isomer.

The cryoscopic constants shown in Table 1 for these two isomers were determined by the addition of a small amount of one isomer to the other.

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* Another 5.7 g of this isomer was separated from the filtrate mentioned above.

** Original Russian pagination. See C.B. translation.

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A POTENTIOMETRIC METHOD FOR THE DIFFERENTIAL TITRATION OF ORGANIC BASES IN A MEDIUM OF METHYL ETHYL KETONE

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Methods of analysis in nonaqueous solvents have their own intrinsic peculiarities and are distinguished by numerous advantages over analysis of aqueous solutions [1]. Thus, for example, many monomeric and polymeric organic compounds are not soluble in water or are hydrolytically decomposed by water. Those water-soluble organic compounds which are not affected by water are weak electrolytes. In particular, organic bases exhibit very weak basic properties, as a rule; their numerical pK values are higher than 10. Therefore, in the majority of cases, titration of organic bases cannot be carried out in aqueous solvents, and is usually carried out in nonaqueous media.

Protogenic solvents such as acetic [1], formic [2], propionic [3], butyric [4], and chloroacetic [5] acids as well as mixtures of these acids with acetic anhydride [6] are usually used as solvents for the titration of organic bases. This stems from the assumption that protogenic solvents increase ionization in accordance with the type of base. Thus, for example, titration of an organic base in a medium of anhydrous formic acid with perchloric acid dissolved in acetic acid can be represented by the following equations:

$$HCOOH + R(Ar)NH_2 \rightleftarrows HCOO^- + R(Ar)NH_3^+;$$

$$HClO_4 + CH_3COOH \rightleftarrows CH_3COOH_2^+ + ClO_4^-;$$

$$R(Ar)NH_3^+ + ClO_4^- \rightarrow [R(Ar)NH_3]^+ClO_4^-;$$

$$\frac{CH_3COOH_2^+ + HCOO^- \rightleftarrows CH_3COOH + HCOOH}{R(Ar)NH_2 + HClO_4 \rightarrow R(Ar)NH_3ClO_4}$$

However, in addition, protogenic solvents have a leveling effect on bases, which makes it impossible to carry out differential titration of mixtures of bases in such media. Moreover, as our investigations showed, it is possible to carry out the differential determination of multicomponent mixtures of bases in ketonic media, and this is of the greatest theoretical and practical interest. Acetonitrile [7], chloroform [8], and methyl isobutyl ketone [9] have been used for differential titration of two-component mixtures of bases.

Solutions of perchloric acid in media of acetic acid or dioxane are usually used for the titration of bases in nonaqueous solvents. We are the first to propose a solution of perchloric acid in methyl ethyl ketone as a titrating agent; this also has significant advantages over all previously used titrating agents.

Experimental

As subjects for our investigation we selected different organic bases including aliphatic and aromatic primary, secondary, and tertiary amines, quaternary ammonium bases, and mixtures of these. Titration of these bases was

carried out in media of anhydrous organic acids, nitriles, ketones, etc. The best results were obtained during titration in ketonic media, which are distinguished by a differentiating effect. Our investigations showed that one of the best differentiating solvents is methyl ethyl ketone. The titration of bases in a medium of methyl ethyl ketone with perchloric acid dissolved in methyl ethyl ketone can be represented by the following equations:

$$CH_3COCH_2CH_3 + R(Ar)NH_2 \rightleftarrows \left[\begin{matrix} O^- \\ | \\ CH_3C = CHCH_3 \end{matrix}\right]^- + R(Ar)NH_3^+;$$

$$HClO_4 + CH_3COCH_2CH_3 \rightleftarrows [CH_3\overset{H^+}{C}OCH_2CH_3]^+ + ClO_4^-;$$

$$R(Ar)NH_3^+ + ClO_4^- \rightarrow [R(Ar)NH_3]^+ ClO_4^-;$$

$$\frac{\left[\begin{matrix} O^- \\ | \\ CH_3C = CHCH_3 \end{matrix}\right]^- + [CH_3COCH_2CH_3]^+ \rightleftarrows 2CH_3COCH_2CH_3}{R(Ar)NH_2 + HClO_4 \rightarrow R(Ar)NH_3ClO_4}.$$

A 0.1 N solution of the titrating agent was prepared by dissolving 8.5 ml of 72% $HClO_4$ in a liter of purified and dried methyl ethyl ketone and saturating the solution with nitrogen over a period of 5 minutes. The drying and purification of the methyl ethyl ketone from acidic impurities was carried out by agitating the ketone with anhydrous potassium carbonate and then distilling. The titer of the solution was established by potentiometric and visual methods using potassium biphthalate in the presence of crystal violet as an indicator. The titer of the solution remained practically constant over the course of a month.

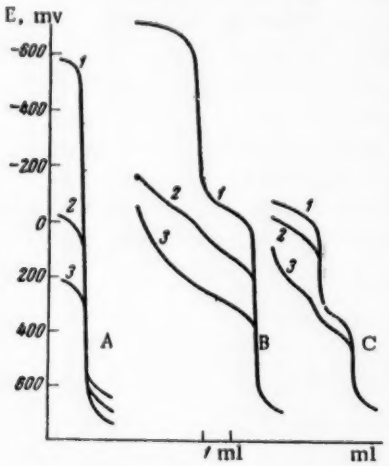

Fig. 1. Potentiometric titration curves for organic bases and their mixtures in a medium of methyl ethyl ketone; A) tetraethylammonium hydroxide with perchloric acid dissolved in: 1) methyl ethyl ketone, 2) dioxane, 3) acetic acid; B) tetraethylammonium hydroxide plus piperidine with perchloric acid dissolved in: 1) methyl ethyl ketone, 2) dioxane, 3) acetic acid; C) piperidine plus acridine with perchloric acid dissolved in: 1) methyl ethyl ketone, 2) dioxane, 3) acetic acid.

Titration of these organic bases and their mixtures was carried out potentiometrically with glass and calomel electrodes. The methyl ethyl ketone, 30 ml, was placed in a 100-ml titration beaker, and dry nitrogen was passed through the liquid. The sample, which weighed 0.02 to 0.05 g, was weighed on an analytical balance and transferred to the beaker for titration. Mixing was accomplished by means of a magnetic stirrer. The titrating solution was added in 0.1-ml portions except in the neighborhood of the equivalent point, where the amount was reduced to 0.02 ml. Titration was continued until the potential reached a maximum and remained relatively constant upon further addition of the titrating agent. The equivalent point was determined from the titration curve.

For purposes of comparison, titrations were carried out with acetic acid and dioxane solutions of perchloric acid, prepared by well-known methods which are described in the literature [10], along with the titrations with the solution of perchloric acid in methyl ethyl ketone.

A comparison of the curves resulting from titration of the individual bases with solutions of perchloric acid in methyl ethyl ketone, dioxane, and acetic acid showed that larger jumps in the titration curve were obtained when the titration was carried out with the solution of $HClO_4$ in methyl ethyl ketone than when the $HClO_4$ was dissolved in dioxane or, especially, acetic acid. Thus, the jump in the curve resulting from the titration of tetraethylammonium hydroxide with $HClO_4$ dissolved in methyl ethyl ketone was 1150 mv (Fig. 1A, 1), while when the dioxane solution was used the jump was 500 mv (Fig. 1A, 2), and with the acetic acid solution it was only 300 mv (Fig. 1A, 3). The increase in the magnitude of the jumps on the titration curves extends the possibility of the differential determination of mixtures of organic bases.

Various multicomponent mixtures of organic bases were titrated with a solution of perchloric acid prepared in methyl ethyl ketone. The

titrations were carried out in a medium of methyl ethyl ketone. Figures 1 and 2 show examples of the titration curves obtained with some of these mixtures of bases. Titration of a mixture of tetraethylammonium hydroxide and piperidine gave a curve (Fig. 1B, 1) with two sharp jumps, which corresponded to the determination of tetraethylammonium hydroxide and piperidine separately. Titrations of this mixture with a dioxane solution (Fig. 1B, 2) and an acetic acid solution (Fig. 1B, 3) of perchloric acid gave curves which were characterized by a single jump. Analysis of these titration curves shows that when a solution of perchloric acid in methyl ethyl ketone was used, differential determination of the mixture of tetraethylammonium hydroxide and piperidine was accomplished, while both bases titrated together when the dioxane and acetic acid solutions of perchloric acid were used. During titration of the mixture of piperidine and acridine (Fig. 1B), curves were obtained which had two sharp jumps, both when the solution of perchloric acid in methyl ethyl ketone was used (Fig. 1B, 1) and when the dioxane solution of perchloric acid was used (Fig. 1B, 2). The first jump corresponds to the neutralization of the piperidine, and the second corresponds to the neutralization of the acridine. Titration with the acetic acid solution of perchloric acid gave a curve (Fig. 1B, 3) on which the first jump, which corresponds to neutralization of the piperidine, was only weakly apparent.

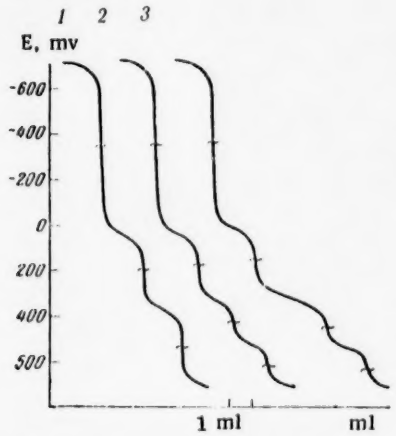

Fig. 2. Potentiometric titration curves for multicomponent mixtures of organic bases in a medium of methyl ethyl ketone: 1) tetraethylammonium hydroxide plus triethylamine plus pyridine; 2) tetraethylammonium hydroxide plus triethylamine plus m-tolylenediamine; 3) tetraethylammonium hydroxide plus tetraethylamine plus pyridine plus m-tolylenediamine.

The results of titrations of three- and four-component mixtures of bases in methyl ethyl ketone are shown in Fig. 2. Titration of a mixture of tetraethylammonium hydroxide, triethylamine, and pyridine gave Curve 1, which has three sharp jumps; the first jump corresponds to neutralization of the tetraethylammonium hydroxide, the second—to neutralization of the triethylamine, and the third—to neutralization of the pyridine. Curve 2 resulted from the titration of a mixture of tetraethylammonium hydroxide, triethylamine, and m-tolylenediamine. Four jumps are apparent on the titration curve; these correspond to separate determinations of the tetraethylammonium hydroxide, triethylamine, and the two amino groups of the diamine molecule.

When pyridine was added to this mixture, we obtained a curve with four jumps [3]. The first jump corresponds to neutralization of the tetraethylammonium hydroxide, the second—to neutralization of the triethylamine, the third—to the simultaneous neutralization of the pyridine and the first amino group of the m-tolylenediamine, and the fourth—to the neutralization of the second amino group of the diamine.

Analysis of the titration curves shows that in a medium of methyl ethyl ketone it is possible to carry out differential titration of multicomponent mixtures of organic bases. This yields curves with sharp titration jumps. Thus, this investigation has shown that the system composed of methyl ethyl ketone and a solution of $HClO_4$ in methyl ethyl ketone can successfully be used for differential determination of organic bases. The error in the determination of individual compounds is ±1%, and that for the determination of the individual components of a mixture is ±2%. This method could find widespread practical use in various scientific research and industrial laboratories.

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THE ATOMIC REFRACTION OF ANTIMONY

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The atomic refraction of phosphorus for the sodium D line has been reliably determined by numerous investigators on the basis of investigations of a large number of organophosphorus compounds [1-6]. The atomic refraction of arsenic has been calculated from data on a few alkyl and mixed alkylaryl organoarsenic compounds [7]. However, there has been no determination of the atomic refraction of either tri- or pentavalent antimony.

In our study of the stereochemistry of organometallic compounds of the ethylene series, we synthesized a number of stereoisomers of propenyl compounds of tri- and pentavalent antimony*, and determined the atomic refractions of antimony from the molar refractions calculated by means of the Lorentz-Lorentz equation.

From a consideration of the values of the atomic refraction of antimony shown in Table 1, it follows that, like the atomic refraction of phosphorus, the atomic refraction of antimony depends on the valence state of the antimony and the nature of the bonds.

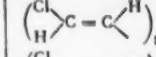
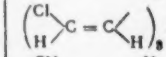
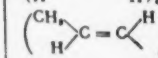
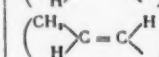
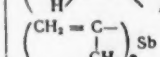
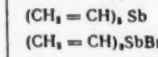
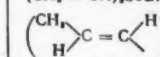
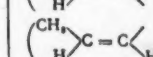
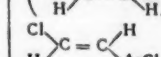
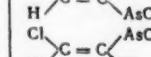
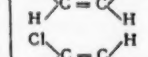
A comparison of the molar refractions of corresponding pairs of cis and trans isomers, specifically, of tripropenylantimony (Nos. 1 and 2), pentapropenylantimony (Nos. 3 and 4), tri-β-chlorovinylantimony (Nos. 5 and 6), dipropenylmercury (Nos. 13 and 14), and β-chlorovinyldichloroarsine (Nos. 15, 16, 17, and 18) leads to the conclusion that trans isomers have higher molar refractions that the corresponding cis isomers. This increased polarizability of trans isomers (as compared to the cis isomers) of alkenyl heteroorganic compounds is in complete agreement with the increased reactivity in the sense of a greater ease of rupture of the C–M bonds, which we have repeatedly pointed out [13-16].

Constants of Alkenyl Compounds of Antimony, Mercury, and Arsenic

Expt. No.	Compound	n_D^t	d_4^t	$t°$	MR	Diff. in mol.refr.	At. refr. of metal
1	$\left(\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C=C<\!\!\begin{matrix}H\\\end{matrix}\right)_3Sb$	1,5511	1,2870	20	60,74	0,32	17,28
2	$\left(\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C=C<\!\!\begin{matrix}\\H\end{matrix}\right)_3Sb$	1,5590	1,3092	20	60,42		16,96
3	$\left(\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C=C<\!\!\begin{matrix}H\\\end{matrix}\right)_5Sb$	1,5490	1,17025	20	88,92	0,45	16,48
4	$\left(\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C=C<\!\!\begin{matrix}\\H\end{matrix}\right)_5Sb$	1,5610	1,1972	20	88,483		16,05

* The synthesis and separation of reaction products of organoantimony compounds was carried out in a stream of dry nitrogen.

Table (continued)

Expt. No.	Compound	n^t_D	d^t_4	t°	MR	Diff. in mol. refr.	At. refr. of metal
5		1,6298	1,7617	50	61,85	0,83	17,54(9)
6		1,6180	1,7580	50	61,02		16,71(9)
7		1,5820	1,5056	20	70,02	—	14,63
8		1,6270	1,8596	20	77,16		15,97
9		1,5475	1,2879	20	60,38	—	16,92
10	$(CH_2=CH)_3Sb$	1,5614	1,4341	20	45,84		16,23
11	$(CH_2=CH)_3Sb$	1,5590	1,2986	20	63,91		14,57
12	$(CH_2=CH)_2SbBr_3$	1,6480	2,1153	20	62,38	—	15,05
13		1,5622	2,2120	20	41,40	0,19	12,43(10)
14		1,5628	2,2297	20	41,21		12,24(10)
15		1,6105	1,8877	20	38,10	0,71	11,43(11)
16		1,5888	1,8682	20	37,39		10,72(11)
17		1,6076	1,8793	25	37,61	0,22	10,94(12)
18		1,5859	1,8598	25	37,39		10,72(12)

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ON THE INTERACTION OF LACTAMS WITH DIACETYLENE

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Original article submitted May 4, 1960

Earlier studies of the interaction of lactams with acetylene have made possible the synthesis of substances which are interesting from both a theoretical and a practical point of view—the vinylactams of the general formula $CH_2=CH-\overline{N(CH_2)_n}\overline{CO}$ [1]. It therefore appeared of interest to study the interaction of lactams with diacetylene, which should yield valuable unsaturated compounds with systems of conjugated multiple bonds in combination with such heteroatoms as oxygen, nitrogen, and sulfur. At the same time, it was of interest to compare the activity of acetylene and diacetylene with respect to reaction with lactams.

The literature provides no information on the interaction of lactams with diacetylene. In the present work, the addition of lactams to diacetylene was studied using pyrrolidone as the lactam. It was found that the reaction proceeds considerably more readily with diacetylene than with acetylene, and it may be carried out at 20-35° and atmospheric pressure. The sodium salt of pyrrolidone serves as the catalyst. The reaction is carried out in a medium of dioxane or benzene, and the process takes place considerably more rapidly in the latter medium. The major reaction product was a crystalline substance with an m. p. of 96.8-97.2° (I) which corresponded in molecular weight and elemental composition to monopyrrolidonylbutadiene. In a number of experiments we were also able to isolate a small amount of an isomeric compound, II, with an m. p. of 78.5-79°. Infrared data* on I and II, which indicated the presence of C=O, C=C, and C≡C groups and the absence of a C=C=C group, showed that, while conceivably possible, the lactim structure ($(\overline{(CH_2)_3-N=C}-O-C_4H_3)$), and the allene and butadiyne structures

$$(\overline{(CH_2)_3 - NH - CO - CH} - CH = C = C = CH_2$$

or $\overline{(CH_2)_3 - NH - C(OH)}\ C \equiv C - C \equiv CH).$

are incorrect.

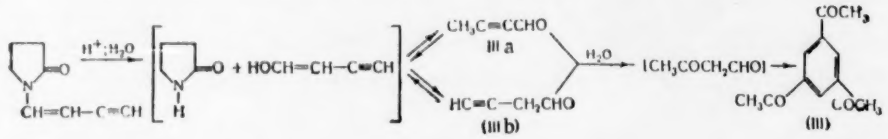
TABLE 1

Infrared Absorption Frequencies of I and II, in cm^{-1}

I	845	948	—	1020	1036	1070	1342	1420	1470	1500	1640	1715	2120
II	844	946	998	1024	—	1068	1344	1408	1468	1490	1638	1728	2120
Group (2)	=CH	C=CH									C=C	C=O	C≡C

* The spectroscopic investigation was carried out by our colleagues T. N. Shurina and B. V. Lopatin of the Optical Laboratory of the Institute of Organic Chemistry Acad. Sci. USSR, for which the authors express their appreciation.

On the other hand, the almost complete agreement of the absorption frequencies suggested that I and II have the same structure. The product of the hydrogenation of I was identical to N-n-butylpyrrolidone (IV) prepared by a well-known method [3, 4] from n-butylamine and γ-butyrolactone, which shows that I was 1-N-(α-pyrrolidonyl)-1-buten-3-yne. This result was confirmed by the preparation of triacetylbenzene (III) by refluxing I with 5% sulfuric acid; the formation of this compound by hydrolysis of 1-substituted 1-buten-3-ynes according to the scheme



has been described in the literature [5, 6].

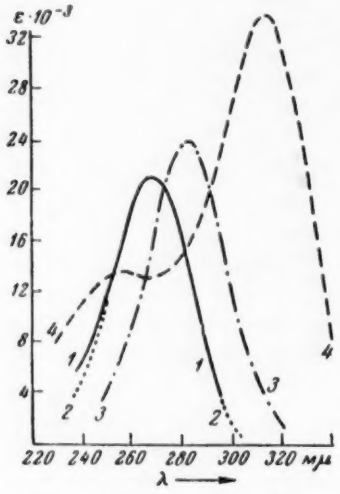


Fig. 1. Ultraviolet absorption spectra (in C_2H_5OH). 1) 1-N-(α-pyrrolidonyl)-1-buten-3-yne (I), 2) 1-N-(α-pyrrolidonyl)-1-buten-3-yne (II), 3) 1-N-(α-pyrrolidonyl)-4-phenylthio-1-buten-3-one (V), 4) 1-N-(α-pyrrolidonyl-4-phenylthio-1,3-butadiene (VIII).

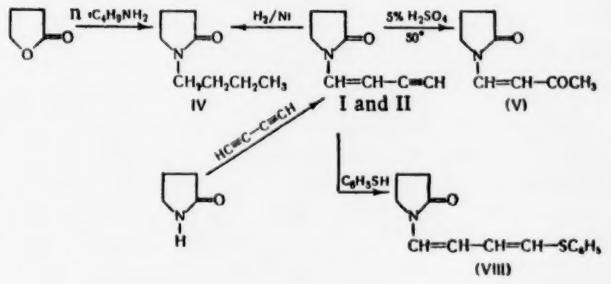
The differences between I and II, in particular, the lower melting point, better solubility in the majority of solvents, and instability of II, can be explained on the basis of cis-trans isomerism or by dimorphism of the crystalline forms. Attempts to isomerize I to II by allowing it to stand in contact with iodine in sunlight for two days and attempts to isomerize II to I by U. V. irradiation for 8 hours ended in failure. In view of these facts and particularly in view of the complete agreement of the U. V. spectra of I and II, which is improbable for geometric isomers, the most probable cause of the differences is monotropic molecular dimorphism.

With the aim of separating the intermediate products (2-butyn-1-al (IIIa) or 3-butyn-1-al (IIIb)) and preventing their trimerization, hydrolysis of I and II was carried out under milder conditions, and the resulting carbonyl compounds were converted to 2,4-dinitrophenylhydrazones (DNPH) by the addition of 2,4-dinitrophenylhydrazine (DNP) directly to the reaction mixture. This led to the isolation of the previously unknown 2,4-DNPH $C_{14}H_{15}N_5O_5$ (VI), m. p. 223.5-224°. During the hydrolysis of I, it was also possible to isolate a small amount of the 2,4-DNPH of 2-butyn-1-al (VII). This investigation showed that (VI) is a derivative of 1-N-(α-pyrrolidonyl)-1-buten-3-one (V), which was formed by hydration of 1-N-(α-pyrrolidonyl)-1-buten-3-yne across the triple bond. Ketone V was isolated during the hydration of I under mild conditions without the introduction of 2,4-dinitrophenylhydrazine into the reaction mixture. The presence of high exaltation of the molar refraction and of a high U. V. absorption maximum in the spectrum of this ketone indicates a high degree of conjugation in the molecule. The infrared spectrum confirmed the structure of V: 1750 cm^{-1}, v.s. (amide C=O); 1682 cm^{-1}, av. (C=O conjugated with C=C); 1632 cm^{-1} and 1608 cm^{-1}, v.s. (C=C); 1464 cm^{-1} w. (—CH_2—); 1396 cm^{-1}, av. gr. (CH_2 in a CH_2—CO—N chain); 1342 cm^{-1}, av.; 1242 cm^{-1}, s.; 1210 cm^{-1} [2].

The remarkable ease with which the triple bond in N-pyrrolidonylbutadiene is hydrated, which is somewhat comparable to the ease of hydration of phenylacetylene [8, 9], is apparently connected with the interaction of the C=O group of the lactam ring with the vinylacetylenic chain through the nitrogen atom. This permitted synthesis of a representative of the previously unknown series of unsaturated ketones with a lactam ring substituted at the double bond. It should also be noted that the reactivity of the double bonds of N-pyrrolidonylbutadiene with respect to hydrolysis was lower than that of the double bonds of alkoxybutenynes [5]; this is analogous to the previously noted lesser reactivity of the double bond of N-vinyllactams with respect to hydrolysis as compared to that of the double bond of vinyl ethers [10].

Like the alkoxybutenynes [4], in the presence of a radical initiator, azobisisobutyronitrile (ABIBN), 1-N-(α-pyrrolidonyl)-1-buten-3-yne adds one molecule of thiophenol with the formation of 1-N-(α-pyrrolidonyl)-4-

phenylthio-1,3-butadiene (VIII). Evidence of this was provided by a negative reaction with Ilosvay's reagent (absence of a C≡CH group) and U. V. spectroscopic data which indicated a long conjugated chain. In the case of radical addition of thiophenol across a double bond, the conjugation chain would be broken. Judging from the broad melting interval, the analytically pure VIII was a mixture of isomers which could not be separated by crystallization.



Experimental

The diacetylene was prepared from 1,4-dichloro-2-butyne [3], and was purified by passage through 10% NaOH and a $CaCl_2$ column. The amount of diacetylene reacted was determined from the weight increase.

1-N-(α-pyrrolidonyl)-1-buten-3-yne (I and II). To a suspension of Na-pyrrolidone, prepared from 2.3 g of pyrrolidone and 0.2 g of sodium in 3 ml of benzene, was added 100 ml of benzene; 6.64 g of diacetylene was absorbed by the suspension at 5° (in a stream of nitrogen). A solution of 6.35 g of pyrrolidone in 4 ml of benzene was added dropwise at 30-35°, and the reaction mixture was allowed to stand at 30-35° for 2 hours and at 20° for 2 days. The product was treated with benzene, and the precipitate was removed by filtration and washed with benzene and ether. From the filtrate was separated 11.4 g of crystals, from which the 1-N-(α-pyrrolidonyl)-1-buten-3-yne was obtained by fractional crystallization (dibutyl ether, 70°): 5.16 g of form I (m. p., 92-95°; 41% yield) and 1.9 g of form II (m. p., 78-85°; 15.2% yield). Repeated recrystallizations yielded I with an m. p. of 96.8-97.2° (from dioxane or benzene) and II with an m. p. of 78.5-79° (from benzene).

I. Found %:	C 70.85, 70.75;	H 6.57, 6.53;	N 10.63, 10.58
II. Found %:	C 70.98, 70.95;	H 6.62, 6.70;	N 10.37, 10.24
C_8H_9NO. Calculated %:	C 71.09;	H 6.70;	N 10.36

Mol. wt.: found (cryoscopically in C_6H_6) 126.4 for I and 119 for II; calculated, 135. A mixed sample of I and II melted at 84-89°. I and II in dioxane solution gave a yellow precipitate with Ilosvay's reagent and a white precipitate with an ammoniacal solution of $AgNO_3$.

Hydrogenation of I. To a hydrogen-saturated (50 ml) suspension of 5.9 g of Raney nickel in 20 ml of dioxane was added a solution of 2.72 g of I in 40 ml of dioxane. Hydrogen was passed into the stirred suspension (23°; 748 mm), and 1136 ml of hydrogen (theoretical, 1042) was absorbed to yield 1.82 g of N-n-butylpyrrolidone (IV). The yield was 64.5%. B. p. 101-101.5°/6 mm, 69-70°/2 mm, n^{20}_D 1.4656, d^{20}_4 0.9599, MR_D found 40.703. N-n-butylpyrrolidone prepared by the interaction of n-butylamine and γ-butyrolactone [5, 6] had a b. p. of 100.5-102.5°/5.5 mm, 68.5-70°/2 mm, n^{20}_D 1.4655, d^{20}_4 0.9595, MR_D: found, 40.707; calculated, 40.66.

Hydrolysis of 1-N (α-pyrrolidonyl)-1-buten-3-yne. 1) A mixture of 0.23 g of I and 2.7 ml of 5.5% sulfuric acid was refluxed for 10 minutes. The precipitate was removed by filtration at 10°, washed with water, and dried; 0.1 g of 1,3,5-trimethylbenzene, m. p. 154-156°, was obtained. The yield was 30%. A mixture with known 1,3,5-triacetylbenzene (m. p. 161-162°) melted at 156.5-159°. 2) A mixture of 4 g of I and 100 ml of 5% sulfuric acid was heated in the presence of hydroquinone for 1 hour at 50-70°. The solution was neutralized with 10% sodium bicarbonate at 10°, saturated with solid ammonium sulfate, and extracted with chloroform. Distillation of the extract yielded: Fraction I, b. p. 80-156°/2 mm, $n^{21.5}_D$ 1.5210, 0.22 g; Fraction II, 156-157°/2 mm, $n^{21.5}_D$ 1.5604, f. p. 12°, 2.35 g of 1-N-(α-pyrrolidonyl)-1-buten-3-one (V). The yield was 51%. A purified

sample of V had an b. p. of 147-147.5°/1.5 mm, f. p. 16°, n^{25}_D 1.5565, d^{25}_4 1.1364, MR_D: found, 43.35; calculated for $C_8H_{11}NO_2F$, 40.44.

	Found %:	C 62.17;	62.16;	H 7.08;	7.26;	N 9.19; 9.03
$C_8H_{11}NO_2$.	Calculated %:	C 62.72;		H 7.23;		N 9.14

2,4-Dinitrophenylhydrazone of the ketone (VI). Bright red crystals, m. p. 223.5-224° (from chloroform).

	Found %:	C 50.44;	50.30;	H 4.56;	4.35;	N 20.91; 20.69
$C_{14}H_{15}N_5O_5$.	Calculated %:	C 50.45;		H 4.54;		N 21.01

3) A solution of 0.4 g of I in 4 ml of 5% sulfuric acid, prepared by heating at 70° for 30 minutes, was added to a mixture of 0.2 g of 2,4-dinitrophenylhydrazine, 2 ml of concentrated sulfuric acid, 2 ml of water, and 4 ml of 96% ethanol. After standing for a day, the mixture was filtered, and the residue was washed with water, alcohol, and ether. This gave 0.25 g of VI, m. p. 211-216°. The yield was 74%. The pure sample melted at 222.5-223.5° (from chloroform) and did not cause depression of the melting point when mixed with a sample of VI obtained in Experiment 2. Treatment of the acid filtrate with water and extraction of the resulting precipitate with ether yielded 0.11 g of yellow crystals with an m. p. of 111-112°. Recrystallization from 96% ethanol gave 0.031 g of the 2,4-dinitrophenylhydrazone of 2-butyn-1-al (VII), m. p. 132-134°. The yield was 13.6%. The literature reports an m. p. of 136° [10]. A mixture of VII with known 2,4-DNPH of 2-butyn-1-al (m. p. 134.5-135°) melted at 132.5-135°. 4) A solution of 0.4 g of II in 4 ml of 5% sulfuric acid, prepared by heating at 45° for 30 minutes, was added to a solution of DNP; further treatment was as in Experiment 3. The resulting VI melted at 222-223°. The yield was 98%, based on the DNP. A mixture with samples of VII prepared in Experiments 2 and 3 showed no depression of the melting point.

1-N-(α-pyrrolidonyl)-4-phenylthio-1,3-butadiene (VIII). To a solution of 2.02 g of I and 0.01 g of ABIBN in 10 ml of dioxane was added 1.79 g of thiophenol, and the mixture was allowed to stand for a week at 20°. The dioxane was distilled, and the residue (3.68 g) was recrystallized to give 1.45 g of VIII, m. p. 94-102.5° (from 96% ethanol). The yield was 39.5%. After recrystallization from dibutyl ether and heptane, the VIII had an m. p. of 98-102.5°.

	Found %:	C 68.83;	69.03;	H 6.26;	6.19;	S 13.00; 13.07
$C_{14}H_{15}NOS$.	Calculated %:	C 68.53;		H 6.16;		S 13.07;

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*Original Russian pagination. See C. B. translation.

COMPLEX FORMATION IN THE SYSTEM $CoCl_2 - HCl - H_2O$

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(Presented by Academician I. I. Chernyaev, May 5, 1960)
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In spite of the large amount of work devoted to the study of complex formation in aqueous solutions of $CoCl_2$ [1-12], information on the composition and on the structure of the complex compounds formed in these solutions is contradictory. There are no quantitative data on the content of complex compounds in the system $CoCl_2-HCl-H_2O$.

The present work constituted an attempt to establish the composition and quantitative content of complex ions of Co(II) in the system $CoCl_2-HCl-H_2O$ with varying concentrations of the components. Identification of the complexes formed in these solutions was accomplished by comparing the electronic absorption spectra of the solutions with the spectra of crystalline complex compounds of Co(II).

Figure 1 shows the closest neighbors of the cobalt ion in crystalline complexes of Co(II); the structure was established by x-ray analysis. The crystal lattice of $[Co(H_2O)_6](ClO_4)_2$ is built up from regular octahedra of $[Co(H_2O)_6]^{+2}$ [13], $[Co(H_2O)_4(ClH_2O)_2]$ complexes form the crystal lattice of $CoCl_2 \cdot 6H_2O$ [14], and the filar and laminated lattices of $CoCl_2 \cdot 2H_2O$ [15] and $CoCl_2$ [16] crystals are constructed from $[CoCl_4(H_2O)_2]$ and $[CoCl_6]$ complexes. Tetrahedral $[CoCl_4]^{-2}$ complexes and Cs^+ ions form the crystal lattice of Cs_2CoCl_4 [1].

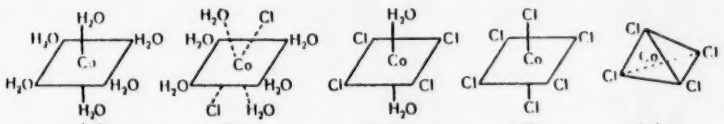

Fig. 1. Structure of inner-sphere complex compounds of Co (II) in crystals: a) $Co(ClO_4)_2 \cdot 6H_2O$; b) $CoCl_2 \cdot 6H_2O$; c) $CoCl_2 \cdot 2H_2O$; d) $CoCl_2$; e) Cs_2CoCl_4.

An article by S. V. Grum-Grzhimailo and I. I. Plyusnina [18] presents data obtained from electronic absorption spectra of $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, $CoCl_2$, and Cs_2CoCl_4, but these spectra were obtained mainly using powdered preparations, and they do not permit calculation of the absorption coefficients of these Co(II) complexes. Moreover, it is impossible to be certain of the uniformity of the chemical compositions of similar preparations when working with finely crystalline samples of crystalline hydrates.

In this connection, using both unpolarized and polarized radiation, we have measured the absorption spectra of thin plates (1 mm-0.01 mm) cut from macrocrystals of $Co(ClO_4)_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, and Cs_2CoCl_4. The measurements were carried out using an SF-11 spectrophotometer. A Franck-Ritter prism was used as the polarizer. Absorption spectra of fine crystals of $CoCl_2$ were measured using a microspectrophotometer, which was kindly loaned to us by M. V. Savost'yanova.

Table 1 shows the wavelengths corresponding to the maxima in the absorption curves of the crystalline Co(II) complexes studied and also the absorption coefficients Co^{+2} calculated per gram-ion for unpolarized radiation. The meaasurements made with polarized radiation showed that pleochroism of the crystals under consideration amounts to a case of "absorption" [19]—a change in the orientation of the crystal was not accomplished by the appearance of new frequencies in its spectrum.

TABLE 1

Wavelengths Corresponding to Absorption Curves of Complex Compounds of Co(II) and Values of the Absorption Coefficients, κ_λ, at the Maxima of the Absorption Curves. Experiment Temperature, 20°.

Crystal	Inner sphere of complex	λ_{max}, mμ, κ_λ, cm^2/g-ion
$Co(ClO_4)_2 \cdot 6H_2O$	$[Co(H_2O)_6]$	$\frac{512^*}{4,2}$
$CoCl_2 \cdot 6H_2O$	$[Co(H_2O)_4(ClH_2O)_2]$	$\frac{470}{1,3}; \frac{505}{3}; \frac{550}{5,2}$
$COCl_2 \cdot 2H_2O$	$[Co(H_2O)_2Cl_4]$	$\frac{516}{6,5}; \frac{620}{4}$
$CoCl_2$	$[CoCl]_6$	530; 580
CS_2CoCl_4	$[CoCl]_4$	$\frac{306}{2,4}; \frac{320}{1}; \frac{380}{0,8}; \frac{412}{1}; \frac{450}{2,2}; \frac{535}{8}; \frac{625}{170}; \frac{660}{190}; \frac{685}{240}$
1 M solution $CoCl_2$ $C_{HCl} < 5$ mole/liter		512—520
1 M solution $CoCl_2$ $C_{HCl} > 5$ mole/liter		304; 320; 380; 414; 450; 535; 625; 660; 685

* The number over the line refers to λ_{max}, that under the line refers to the corresponding κ_λ.

Absorption spectra of aqueous solutions of $CoCl_2$ containing HCl were studied at $CoCl_2$ concentrations of 1 mole/liter, 0.1 mole/liter, 0.01 mole/liter, and 0.001 mole/liter, and the HCl concentration in each series of experiments was varied from 0 to 11 moles/liter; the temperature was 20°C.

In all cases where the concentration of HCl in the solution was from 0 to 4 moles/liter, the spectra had only an absorption band at 515 mμ, which was identical to the absorption band of the $[Co(H_2O)_6]^{+2}$ ion in the spectrum of the crystalline hydrate $Co(ClO_4)_2 \cdot 6H_2O$. At an HCl concentration of 4 moles/liter, the absorption spectrum of the $CoCl_2$ solution contained numerous absorption bands, which agreed exactly with the absorption bands of the $[CoCl_4]^{-2}$ complex in a Cs_2CoCl_4 crystal. With an increase in HCl concentration, the absorption band at 515 mμ shifted to 535 mμ, which is readily explained by overlapping of the absorption bands of $[CoCl_4]^{-2}$ and $[Co(H_2O)_6]^{+2}$. No frequencies corresponding to the complexes $[Co(H_2O)_4(ClH_2O)_2]$ and $[CoCl_6]$ were observed in the spectra of solutions of $CoCl_2$ in HCl.

The absorption bands of the $[CoCl_4(H_2O)_2]^{-2}$ ion, which are located at 516 mμ and 620 mμ, overlapped with the corresponding absorption bands of $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ complexes. In addition, the crystalline hydrate $CoCl_2 \cdot 2H_2O$, in which the closest neighbors of the Co^{+2} ion are four Cl^- ions and two H_2O molecules, had a strong maximum at $\lambda = 280-290$ mμ. The absorption coefficient of this crystalline hydrate at $\lambda = 280$ mμ was 10-15 times higher than the absorption coefficients of $Co(ClO_4)_2 \cdot 6H_2O$ and Cs_2CoCl_4 crystals. Measurements were also carried out to determine the optical densities of solutions of $CoCl_2$ in HCl with varying concentrations of the latter; these showed that appreciable amounts of $[CoCl_4 \cdot (H_2O)_2]^{-2}$ complexes were absent.

To a first approximation, it may be assumed that when $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ ions transfer from the crystalline phase to solution, the absorption coefficients of these ions do not undergo significant change.

A comparison of the absorption curves of the crystalline hydrate $Co(ClO_4)_2 \cdot 6H_2O$ and dilute aqueous solutions of Co(II) salts supports this assumption.

Though the absorption coefficients of the $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ ions were measured for the crystalline phase, it seemed reasonable to calculate the approximate concentrations of these ions from the optical densities of $CoCl_2$ solutions. The data obtained from these calculations are of the nature of estimates and are presented in Table 2.

TABLE 2

Distribution of Co^{+2} Ions between Complex Compounds in the System $CoCl_2 - HCl - H_2O$ at Varying $CoCl_2$ and HCl Concentrations and a Temperature of 20° (in percent).

HCl concentration mole/liter	$CoCl_2$ concentration in the solution, mole/liter							
	1		0.1		0.01		0.001	
	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$	$[Co(H_2O)_6]^{+2}$	$[CoCl_4]^{-2}$
0	100	0	100	0	100	0	100	0
4	95	5	100	0	100	0	100	0
5	80	20	98	2	99	1	100	0
6	60	40	90	10	90	10	92	8
7	45	55	65	35	70	30	80	20
8	30	70	35	65	40	60	55	45
9	10	90	20	80	25	75	35	65
10			15	85	20	80	25	75
11			10	90	15	85	20	80

Replacement of H_2O molecules in the hydrate shell of the Co^{+2} ion by Cl^- ions proceeded to a significant extent only at high HCl concentrations in the solution. The degree of dissociation of HCl is low at such concentrations. This suggests that the process $[Co(H_2O)_6]^{+2} + 4Cl^- = [CoCl_4]^{-2} + 6H_2O$ proceeds only if there is in the solution a significant amount of undissociated HCl molecules, which act as a dehydrating agent.

A similar assumption found confirmation in the fact that the concentration of $[CoCl_4]^{-2}$ ions in the system $CoCl_2 - HCl - H_2O$ increased when acetone or sulfuric acid was introduced into the solution.

In this connection, a high strength may be assumed for bonds of the Co^{+2} ions with H_2O molecules, which are formed with its closest neighbors in aqueous solutions; this is in agreement with literature data on the energy of addition of water to the Co^{+2} cation [20, 21].

The circumstance that the electronic absorption spectra of $CoCl_2 - HCl - H_2O$ systems showed only the frequencies of $[Co(H_2O)_6]^{+2}$ and $[CoCl_4]^{-2}$ complex ions can be explained as follows: Either the process of replacement of H_2O molecules in a $[Co(H_2O)_6]^{+2}$ ion by Cl^- ions, which is accompanied by a change in the coordination number of Co(II), proceeds stepwise without the formation of intermediate complex compounds, or this process proceeds in several stages but the concentration of intermediate complexes is very small.

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THE THERMODYNAMICS OF THE THERMAL TRANSFORMATION OF KAOLINITE

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Though there can be no doubt as to the validity of the position that, as in all chemical processes, the change occurring in kaolinite during heating [1,2] is governed by the laws of thermodynamics and kinetics, the predominant portion of the work carried out up to the present time has been devoted to the second of these fields; this is particularly true of work carried out over a range of temperatures.

The small number of investigations [2-4] of the thermodynamics of the process has been limited by the conclusion that during the synthesis of mullite from the oxides at an A:S ratio of 1:1, the primary product is necessarily mullite ($\Delta F_{1200^\circ K} = -66\,810$ cal/mole), but with an increase in temperature, the thermodynamic possibility of obtaining sillimanite increases ($\Delta F^{A_3S_2}_{2000^\circ K} = -52\,170$ cal/mole and $\Delta F^{AS}_{2000^\circ K} = -52\,300$ cal/mole). At an A:S ratio of 3:2, mullite is the more probable over the entire temperature interval ($\Delta F_{1000^\circ K} = -229\,490$; $\Delta F_{1800^\circ K} = -163\,880$ cal/mole, while for sillimanite at these temperatures, $\Delta F_{1000^\circ K} = -118\,800$ cal/mole and $\Delta F_{1800^\circ K} = -102{,}860$ cal/mole.

Up to the present, data for metakaolin ($\Delta H_{298.16^\circ K} = -767\,500$ cal/mole, $\Delta F_{298.16^\circ K} = -719\,410$ cal/mole) have been used in thermodynamic calculations of kaolinite transformations. In this case, mullite is the most probable over the entire temperature interval ($\Delta F_{1000^\circ K} = -104\,740$ cal/mole, $\Delta F_{1600^\circ K} = -96240$ cal/mole). The formation of mullite from metakaolin takes place with a higher free energy change ($\Delta F_{1800^\circ K} = -203{,}020$ cal/mole) when alumina is added than when it is not, and the preferred compound in this case is again mullite ($\Delta F^{A_3S_2}_{1800^\circ K} = -203{,}020$ cal/mole, and $\Delta F^{AS}_{1800^\circ K} = -141{,}220$ cal/mole for the formation of sillimanite).

The calculations can be made by another method. In this case, using both well-known and recent data [5-7] it is possible to start with kaolinite (see Table 1). The heat capacity was determined by the additive method from the oxides and water [8].

The following reactions were considered on the basis of the data presented in Table 1:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \text{ vapor;} \quad (1)$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot SiO_2 + SiO_2 + 2H_2O \text{ vapor;} \quad (2)$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow \alpha Al_2O_3 + 2SiO_2 + 2H_2O \text{ vapor;} \quad (3)$$

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow \frac{1}{3}(3Al_2O_3 \cdot 2SiO_2) + \frac{4}{3} SiO_2 + 2H_2O \text{ vapor.} \quad (4)$$

The following equations were obtained for the above reactions:

$$\Delta F = +80814 - 11{,}72T \cdot \ln T + 10{,}69 \cdot 10^{-3}T^2 - 2{,}27 \cdot 10^5 T^{-1} - 22{,}6T; \quad (1)$$

$$\Delta F = -9605 - 10{,}33T \cdot \ln T + 7{,}99 \cdot 10^{-3}T^2 + 3{,}38 \cdot 10^5 T^{-1} - 26{,}02T; \quad (2)$$

$$\Delta F = +35964 - 6{,}74T \cdot \ln T + 5{,}36 \cdot 10^{-3}T^2 + 2{,}92 \cdot 10^5 T^{-1} - 46{,}4T; \quad (3)$$

$$\Delta F = -26712 + 0{,}09T \cdot \ln T + 6{,}3 \cdot 10^{-3}T^2 + 1{,}95 \cdot 10^5 T^{-1} - 93{,}85T. \quad (4)$$

The results of calculations by means of these equations are shown in Fig. 1.

TABLE 1

Expt. No.	Compound	S_{298}	ΔH	ΔF	$c_p = f(T)$
1	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	40,5	—964,94	—883,0	$c_p = 57,47 + 35,3 \cdot 10^{-3} \cdot T - 7,87 \cdot 10^5 \cdot T^{-2}$
2	$Al_2O_3 \cdot SiO_2$ (sil.)	27,0	—648,9	—615,0	$c_p = 42,24 + 6,0 \cdot 10^{-3} \cdot T - 12,1 \cdot 10^5 \cdot T^{-2}$
3	$3Al_2O_3 \cdot 2SiO_2$	60,0	—1804,0	—1712,5	$c_p = 84,22 + 20,0 \cdot 10^{-3} \cdot T - 25,0 \cdot 10^5 \cdot T^{-2}$
4	$Al_2O_3 \cdot 2SiO_2$	32,78	—767,5	—719,41	$c_p = 54,85 + 8,8 \cdot 10^{-3} \cdot T - 3,48 \cdot 10^5 \cdot T^{-2}$
5	γ-Al_2O_3	12,186	—384,84	—	$c_p = 16,37 + 11,1 \cdot 10^{-3} \cdot T$
6	α-Al_2O_3	12,186	—399,09	—376,77	$c_p = 27,43 + 3,06 \cdot 10^{-3} \cdot T - 8,47 \cdot 10^5 \cdot T^{-2}$
7	SiO_2-β q.	10,0	—205,4	—192,4	$c_p = 11,22 + 8,2 \cdot 10^{-3} \cdot T - 2,7 \cdot 10^5 \cdot T^{-2}$
8	SiO_2-α q.	—	—205,62	—192,33	$c_p = 14,41 + 1,94 \cdot 10^{-3} \cdot T$
9	SiO_2-α trid.	10,36	—204,80	—191,9	$c_p = 13,64 + 2,64 \cdot 10^{-3} \cdot T$
10	SiO_2-α cris.	10,29	—205,0	—192,1	$c_p = 14,40 + 2,04 \cdot 10^{-3} \cdot T$
11	H_2O-liq.	16,72	—68,32	—56,69	$c_p = 7,93 + 16,95 \cdot 10^{-3} \cdot T + 2,67 \cdot 10^5 \cdot T^{-2}$
12	H_2O vap.	45,13	—57,80	—54,64	$c_p = 7,17 + 2,56 \cdot 10^{-3} \cdot T + 0,08 \cdot 10^5 \cdot T^{-2}$

It should be remarked that the accuracy of the calculations is dependent on the accuracy of the currently available initial data.

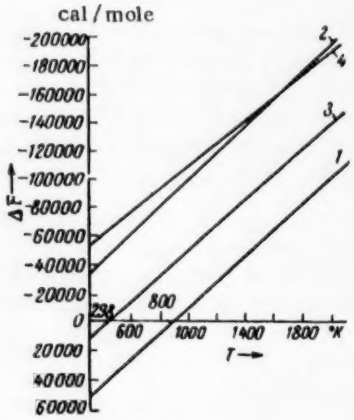

Fig. 1.

The results of the calculations are interesting, first of all because they provide for the first time a thermodynamic basis for the appearance of metakaolin at a temperature of about 900° K (600° C). It thus becomes clear that no length of heating below this temperature limit will produce metakaolin.

Secondly, the results are interesting in that the lines for Reactions 2 and 4 lie very close together; i.e., sillimanite and mullite have almost equal thermodynamic probabilities of being formed. Apparently, the appearance of one compound or the other will be determined by kinetic factors and, in particular, the degree of crystallization of the original kaolinite.

This opinion is in complete agreement with recent opinions [9, 10] on the process occurring when kaolinite is heated, and these, in turn, agree to a considerable extent with our earlier considerations [1] and with our interpretation of the first exothermic reaction [1,2].

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ON THE STRUCTURE OF THE COMPLEX ION $[OsNCl_5]^{2-}$

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The structure of K_2OsNCl_5 and $KOsNBr_4 \cdot 2H_2O$ crystals have been investigated by T. B. Bokii, L. O. Atovmyan and T. S. Khodasheva [1], who found that in the octahedral complex ions $[OsNCl_5]^{-2}$ and $[OsNBr_4(H_2O)]^-$ the Os-N distance is very short (~ 1.60 A) and that in the first of these ions the Os-Cl distances are not equal—the four chlorine atoms in the equatorial plane have bond lengths of 2.4 A, which is close to the sum of the covalent radii, while the distance to the fifth chlorine atom (which is trans to the nitrogen atom) is considerably shortened (2.1 A). Moreover, in the $[OsNBr_4(H_2O)]^-$ ion, the distance to the water molecule, which is trans to the nitrogen atom, is normal.

TABLE 1

Assignment of the Atomic Orbitals of the Central Atom and Orbitals of the Ligands to Identical Representations of Space Group C_{4V}.

Orbital	Identical Representation				
	A_1	A_2	B_1	B_2	E
Atomic orbitals of central atom	s, p_z, d_{z^2}	—	$d_{x^2-y^2}$	d_{xy}	p_x, p_y d_{xz}, d_{yz}
σ-Orbitals of the 4 Cl atoms in the equatorial plane	σ_1		σ_2		σ_3, σ_4
Orbitals of the N atom	$\sigma(p_z)\,\sigma_N$ $\pi(p_x, p)_y$				π_{N_1}, π_{N_2}
Orbitals of the Cl atom trans to the N atom	$\sigma(p_z)\,\sigma_{Cl}$ $\delta(d_{xy})$			δ_{Cl}	

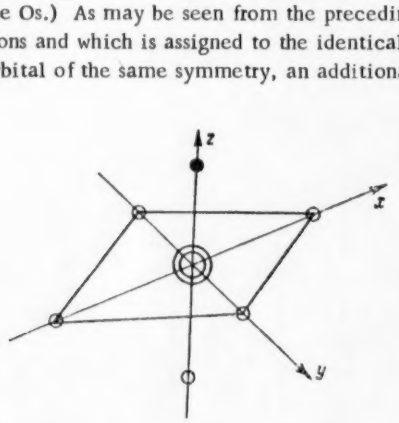
In order to clear up the anomalies observed among the bonds in $[OsNCl_5]^{2-}$, we applied group theory in a consideration of the possible bonds formed between the central atom and the ligands in this complex ion. The structure of the $[OsNCl_5]^{2-}$ ion, which belongs to space group C_{4V}, is shown in Fig. 1. We took the C_4 axis as the z axis, thereby making it coincide with the line NOsCl, and ClOsCl lines in the equatorial plane were taken as the x and y axes. Table 1 presents the assignment of atomic orbitals of the central atom and orbitals of the ligands to identical representations of the symmetry group. The σ-orbitals of the four Cl atoms in the equatorial plane are formed from the p_x-orbitals of the two Cl atoms located on the x axis and the p_y-orbitals of the two Cl atoms on the y axis. As an inspection of Table 1 reveals, these orbitals interact with the $d_{x^2-y^2}sp_xp_y$-orbitals of the Os with the formation of four Os-Cl σ-bonds with a square configuration. In addition to these σ-bonds,

there are two other σ-bonds formed between Os and its ligands; these are along the z axis, and are formed by the p_z-orbitals of the N and Cl and the hybrid $p_z d_{z^2}$ orbitals of the Os. The selection of orbitals for these σ-bonds is unequivocal. The other d-orbitals are not suitable for the formation of σ-bonds. However, the formation of only these σ-bonds does not exhaust the possibilities for the formation of bonds between the Os and its ligands, since the nitrogen still has two unpaired electrons (in p_x and p_y orbitals, E symmetry) which can form the two π bonds with the d_{xz}- and d_{yz}-orbitals of the Os (type dπ-pπ), so that the Os-N bond is a triple bond. Precisely this is the reason for the short distance between the Os and the N. In this case, only d_{xz} and d_{yz} orbitals can be used for the second and third components of the Os bond.

The formation of all of the bonds described above requires the presence at the Os atom of eight unpaired electrons in the orbitals $d_{x^2-y^2} sp_x p_y p_z d_{z^2}$ (for the σ-bonds) and d_{xz}, d_{yz} (for the π-bonds with the N). Moreover, if each of the Cl atoms and the N form one and three bonds, respectively, with the Os, the charge on the complex ion (−2) represents a formal charge on the Os atom *. At the same time, the Os atom is in a state which provides for the formation of all of the bonds enumerated.

	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2-y^2}$	s	p_x	p_y	p_z
Os^{2-}	↓↑	↓	↓	↓	↓	↓	↓	↓	↓
		π-bonds with N		σ-bonds with N and Cl in trans position	σ-bonds with Cl in equatorial plane				σ-bonds with N and Cl in trans position

Usually, a consideration of the bonds in Os complexes containing a nitrogen atom is limited by the above considerations concerning the formation of ordinary bonds between the Os and all Cl atoms and the Os ≡ N triple bond. However, this does not provide an explanation of the difference between the Os-Cl distances in the equatorial plane and that along the z axis. We propose that it is possible to arrive at an explanation of this difference if one takes into account the possibility of the formation of additional bonds between the Cl atoms and the central atom by means of the unshared pair of electrons of the Os and the free d-orbitals of the Cl in the trans position. (We have not considered the possibility of the formation of a π-bond by means of the unshared pairs of p electrons of the Cl atoms and free orbitals of the central atom in view of the lack of free orbitals at the Os.) As may be seen from the preceding, the Os still has a d_{xy} orbital which is occupied by a pair of electrons and which is assigned to the identical representation B_2. This implies that if the Cl_{trans} atom has an empty orbital of the same symmetry, an additional bond can be formed between the Os and Cl. All 3d-orbitals of the Cl atom are empty, but of these only the $3d_{xy}$-orbital belongs to the identical representation B_2 (with C_{4v} symmetry of the complex ion). Three types of bonds are possible in principle between the d_{xy}-orbitals of the two interacting atoms: σ (with overlap of two loops of the functions, one from each orbital), π (with overlap of four loops, two from each orbital), and δ (with overlap of all eight loops) [2]. In our case, the two d_{xy}-orbitals (of the Os and Cl atoms) are disposed in parallel planes. Hence, overlapping of them is possible only with the formation of a bond of the δ type, and conditions for the formation of σ or π bonds are considerably less suitable.



◎-Os atom ●-N atom ○ Cl atom

Fig. 1.

δ Bonds cannot be formed with the Cl atoms in the plane, since the required Os orbitals (d_{xy} and d_{yz}) are already occupied in the multiple bond with the N. In the octahedral complexes $OsCl_6^{2-}$ and $OsBr_6^{2-}$, the formation of δ bonds is equally probable with any of the halogen atoms along all three axes, x, y, and z. But the central atom can supply one one pair of electrons for these bonds (in these complexes, two electrons of the Os remain unpaired), so that each Os-Cl bond has 1/6 of a δ bond. Thus, in $OsNCl_5^{2-}$ the Os-Cl bonds in the plane are purely ordinary, while in $OsCl_6^{2-}$ the Os-Cl bonds have a slight δ-bond character. Therefore, bonds of these two types are of close to the same length.

* As a consequence of the partial ionic character of the Os-Cl bonds and the Os-N π-bonds, the charge is actually distributed over all atoms, but this is not essential for a group theory consideration of the possibility of bond formation.

In contrast to the preceding, the Os-Cl_{trans} bond in $OsNCl_5^{2-}$ is multiple, consisting of σ and δ components. The presence in this bond of the additional δ component is, in our opinion, the reason for the shortening of this distance.

The condition for the emergence of an additional bond between the Os atom and the atom in the trans position to the N is the presence at the trans atom of a free d_{xy}-orbital (with C_{4V} symmetry, an s or p orbital does not belong to identical representation B_2, to which the Os orbital not used in the σ bonds and the π bond with the N belongs). Such an orbital, which has almost the same energy as the orbitals occupied in the bonds, can be present only in atoms of the third period of the Mendeleev Periodic System, and not in atoms of the second period. Therefore, while Cl can form an additional bond with the Os atom, F and O atoms cannot form such a bond, and the Os-O bond in $[OsNBr_4OH_2]^-$ and the Os-F bond in $[OsNF_5]^{2-}$ must simply be ordinary bonds. This conclusion is in agreement with the conclusion that, according to the data of reference [1], the Os-O distance in $[OsNBr_4OH_2]^-$ is normal. It may also be assumed that the Os-F_{trans} distance in $[OsNF_5]^{2-}$ does not differ appreciably from the remaining Os-F distances.

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*Original Russian pagination. See C. B. translation.

INVESTIGATION OF THE CONFIGURATIONS OF SATURATED SYSTEMS BY NUCLEAR MAGNETIC RESONANCE. 2-METHYL-1-HYDROXYCYCLOHEXYLETHYLENE OXIDE AND SOME 1-HYDROXYDECALYLETHYLENE OXIDES

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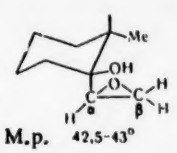
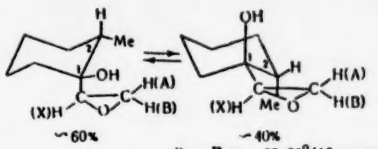
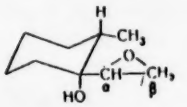
On the basis of chemical experiments and the concepts of conformation analysis, one of us together with Nazarov and co-workers [1-4] established the configurations of a number of derivatives of cyclohexane and decalin. Somewhat later, the configurations of the cyclohexane derivatives were confirmed by means of Raman spectroscopy [5]. At that time, the predominant conformations of these compounds, which exist in an equilibrium mixture with their



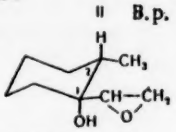
M.p. 42.5-43°



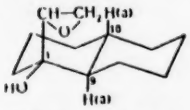
II B.p. 88-89°/10 mm



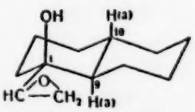
III M.p. 75-75.5°



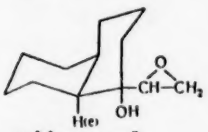
IV M.p. 40.5-41°



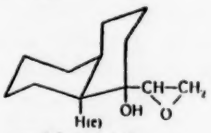
V M.p. 112-112.5°



VI M.p. 116.5-117.5°



VII M.p. 100-101°



VIII M.p. 88-90°

rotational isomers, were determined, and generalizations were formed regarding the stereochemistry of nucleophilic addition across the carbonyl group of 2-substituted cyclohexanones and cis- and trans-decalones [6]. It was, therefore, of considerable interest to investigate the configurations of these compounds by the method of nuclear magnetic resonance (n.m.r.), a method which possesses high resolution. The present article presents the results of an investigation of the n.m.r. spectra of four cyclohexane derivatives (I-IV) and four decalin derivatives (V-VIII). The spectra were obtained by one of us [7] in the physics laboratory of Harvard University, U.S.A. In all of the compounds investigated, one of the substituents was ethylene oxide. Most spectra were obtained at Harvard University using a Varian n.m.r. spectrometer at a fixed frequency of 40 Mcps, and the remaining spectra were obtained at Mellon Institute at a fixed frequency of 60 Mcps. The substances were investigated in solution in carbon tetrachloride; hexamethyldisiloxane was used as an internal reference. Chemical shifts and frequency splitting were determined with an accuracy of 0.3-0.7 Mcps.

The hydrogen atoms of the ethylene oxide ring constituted the major field of investigation in the present work. These atoms differed with respect to their positions; one of the two hydrogen atoms at the β-carbon atom of the oxide ring was in the cis and the other was in the trans position with respect to the hydrogen atom at the α-carbon atom of the oxide ring. These three atoms can be considered as a system of three interacting spins.

In accordance with reference [8], we shall denote by A, B, and C nonequivalent nuclei of the same species, the chemical shift of which is of the same order of magnitude as that due to spin-spin interaction. We shall denote by X, Y, Z. . . another series of nuclei, the signals of which are not so close to the A, B, C . . . signals. The nuclei of the X, Y, Z. . . series may or may not be of the same species as A, B, C. . . It was of paramount importance to us that the chemical shift between the A, B, C. . . and X, Y, Z. . . groups was great in comparison to the spin-spin interaction. In this case, symbols for interaction in a system of three spins may be written as A_3, AB_2, AX_2, ABX, etc. In general, visual analysis of the spectrum of such a system makes it possible to determine qualitatively to which type of these interactions the system under investigation belongs. Thus, in our case (see Fig. 1 and Table 1), compounds I, V, VII, VIII, and one of the conformations of compound II (see below) are characterized by interactions of the AB_2 type. Further, for systems of three spins of the type of hydrogen atoms attached to an ethylene oxide ring, it has been found [9] that if it is not attached to the cyclohexane ring or orientated axially to it, the spectrum will be of the ABX type with an octet for the AB frequencies and a quartet or overlapping quartet for the X frequencies. If the ethylene oxide ring is oriented equatorially to the ring, a characteristic AB_2 spectrum (an octet with more or less splitting of the frequencies, see Fig. 1 and Table 1) is obtained. Thus, in compounds I, V, VII, VIII, and one of the conformations of II (see below), the ethylene oxide ring is disposed axially, while in compounds III, IV, VI, and one of the conformations of II (see below), the ethylene oxide ring is disposed equatorially. In the case of the ABX spectrum, the frequencies of the X hydrogen atom, which is attached to the α-carbon atom of the ethylene oxide ring, were located on the low side of the field; the A hydrogen atom with a higher coupling constant is cis with respect to the X hydrogen, and its frequencies are on the low side of the field [9]. In the case of the AB_2 spectrum, the frequencies of the A hydrogen atom are apparently located on the low side of the field as compared to the frequencies of the B hydrogen atoms; the A hydrogen atom is (judging from the higher values of the spin interaction constants in the majority of cases) one of the β-hydrogen atoms, specifically, the one in the cis position with respect to the hydrogen at the α-carbon atom; the remaining two hydrogen atoms, which are in trans positions, are magnetically equivalent, and their frequencies are on the high side of the field. The relative positions of hydrogen atoms, A, B, X in the system ABX and of atoms A, B, B in the system AB_2 relative to the hydrogen atoms of the ethylene oxide ring are indicated in conformity with the above by means of A, B, and X placed by the H symbols for the hydrogen atoms of the ring in the representation of compound II shown at the beginning of the article. The chemical shifts and the spin coupling constants were evaluated approximately using the appropriate representation and tables for AB_2 and ABX [8], which are reproduced as Table 2. Axial and equatorial positions of the ethylene oxide ring in the conformations are denoted by (a) and (e), respectively. In the n.m.r. spectrum of compound II were observed more than 12 of the theoretically possible peaks for an ABX-type system of hydrogen atoms of an ethylene oxide ring. In addition, in the n.m.r. spectrum of the methyl group of compound II were observed four peaks (two doublets) instead of the two peaks (one doublet) which would be expected if there was only one type of methyl group in the compound. This circumstance and the course of the chemical reaction during the preparation of compound II force us to propose that compound II exists as an equilibrium mixture of two conformations: a conformation with an axial posi-

TABLE 1

Peaks Observed for Protons of the Ethylene Oxide Ring; at 40 Mcps

Compound	δ_8*	AB								X		
		8	7	6	5	4	3	2	1	12	11 and 10	9
I	97,2	0	3,65	5,83	9,82	9,82	13,88	16,82	19,80	19,80	23,30	27,17
II **	100,0											
V	101,3	0	3,69	6,17	10,0	10,0	13,42	16,30	19,43	21,48	24,92	28,15
VII	97,4	0	3,62	5,37	8,37	8,37	11,21	13,90	16,95	30,0	33,5	36,9
VIII	97,2	0	3,92	5,87	10,17	10,17	13,59	16,59	19,89	30,8	34,3	37,94
	δ_3*	8	7	6	5	4	3	2	1			
II **	110,0											
III	111,1	—	−10,86	−6,74	−6,74	−4,34	0	5,2	—			
IV	113,2	−13,7	−9,35	−9,35	−9,35	−3,60	0	3,5	—			
V	112,0	—	−9,25	−6,45	−5,35	−3,40	0	4,75	—			

* Chemical shifts 8 and 3 of the peaks at 40 Mcps are referred to hexamethyldisiloxane with a positive sign for the low side of the field.

** The chemical shifts for II were determined at 60 Mcps and are multiplied by a correction coefficient of 2/3.

TABLE 2

Calculated Parameters for the Ethylene Oxide Ring (cps)

Compound	Conformation*	J_{AB}		J_{AX}		J_{BX}		$\delta = \nu_B - \nu_A$		$\delta = \nu_A - \nu_X$		$\frac{J_{AB}}{\delta_{AB_e}}$
		60 Mcps	40 Mcps	60 Mcps	40 Mcps	60 Mcps	40 Mcps	60 Mcps	40 Mcps	60 Mcps	40 Mcps	
I	a	—	6,0	—	4,2	—	3,1	—	8,7	—	18,0	—
II	e	4,4	—	—	—	—	—	−11	—	—	—	0,4
	a	5,3	—	2,8	—	2,8	—	11,3	—	21,6	—	—
III	e	6,2	7,5	—	—	—	—	−10,3	−8,3	—	—	0,6
IV	e	—	6,8	—	—	—	—	—	−11,3	—	—	0,4
V	a	5,6	6,2	3,6	3,7	2,8	3,0	11,4	7,6	26,6	18,9	—
VI	e	5,4	6,5	—	—	—	—	−9	−7,1	—	—	0,6
VII	a	5,5	5,5	3,7	4,0	2,8	2,9	8,9	5,8	41,2	28,2	—
VIII	a	5,5	6,1	4,1	2,3	2,5	2,9	10,7	8,1	37,7	28,7	—

* Position of the ethylene oxide ring in the molecule.

tion of the ethylene oxide ring, which is characterized by a spectrum of the type ABX with 12 peaks, and a conformation with an equatorial position of the ethylene ring, which is characterized by a spectrum of the type AB_2 with eight peaks.

In the n.m.r. spectrum of compound I there were 12 frequencies due to hydrogen atoms of the ethylene oxide ring, which is characteristic of an ABX system with an axial position of the oxide ring. On the basis of general considerations, it may be assumed that this configuration differs from the configuration of compound II, which also has an axial oxide ring, by a different position of the oxide ring; specifically, in I the oxygen atom of the ring is located so that it interacts with the equatorial hydroxyl (hydrogen bond). This isomer is more stable and is characterized by a higher melting point than compound II, in which the predominant conformation has the ring in an axial position also. Table 2 presents values of the ratio $I_{AB}/(\delta=(\nu_B-\nu_A))$ for conformations with an equatorial ethylene oxide ring; the measurements were made at 60 Mcps. This ratio is 0.4 for compounds II and IV, while it is 0.6 for compound III. The equal values of this ratio for one of the conformations of compound II and for compound IV are apparently due to an equivalent position of the ethylene oxide ring in these compounds; the position of the ring is different in compound III, which has a higher melting point (see scheme at the beginning of the article). It is well known that the n.m.r. spectra of cis- and trans-decalins differ sharply; the cis isomer is character-

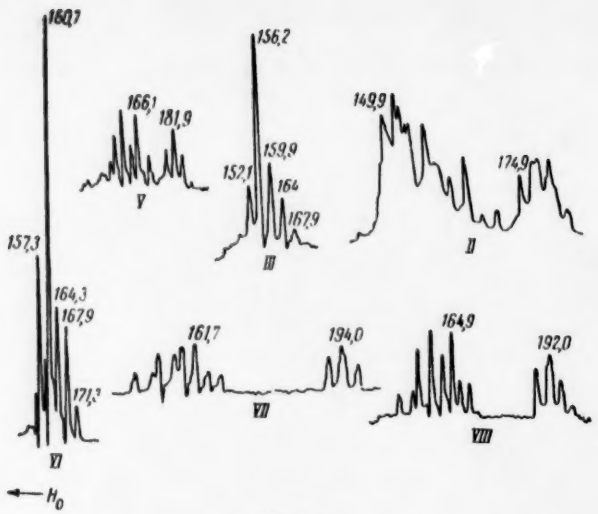


Fig. 1.

ized by a sharp peak, while the trans isomer has a doubly peaked broad band [8]. On the basis of our study of the n.m.r. spectra, we feel that decalols V and VI belong to the trans-decalin series, and decalols VII and VIII belong to the cis-decalin series. The n.m.r. spectrum of decalol VI belongs to type AB_2 (see Fig. 1 and Table 1) and, consequently, its ethylene oxide ring occupies an equatorial position (see above). The n.m.r. spectrum of decalol V belongs to type ABX (see Fig. 1 and Table 1), and, consequently (see above), its ethylene oxide ring is axial. It follows from this that the configurations of compounds V and VI, which were previously assigned on the basis of incomplete chemical data [4], should be reversed. The ratio $I_{AB}/(\delta = (\nu_B - \nu_A))$ for decalol VI (see Table 2) is the same as for compound III. On this basis, we consider it probable that the position of the ethylene oxide ring in configuration VI is the same as in III. According to the relative positions of H_9 and the ethylene oxide ring, compound VI is cis-ae, and compound V is trans-aa. Decalols VII and VIII have n.m.r. spectra of the type ABX (see Fig. 1 and Table 1), and, consequently, their ethylene oxide rings are axial. The difference in VII and VIII is apparently due to erythrothreo isomerism of the oxide ring.

Our thanks are due Dr. A. A. Bothner-By and B. L. Shapiro of the Mellon Institute for making it possible for us to obtain the n.m.r. spectra of the compounds at 60 Mcps in their laboratory, to Prof. R. V. Pound and M. I. Batuev for fruitful discussions of the results, and to G. V. Aleksandrova and A. V. Kamernitskii for the gift of samples of the compounds.

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ON THE PREPARATION OF RHENIUM HEXAFLUORIDE BY FLUORINATION OF THE METAL WITH CHLORINE TRIFLUORIDE

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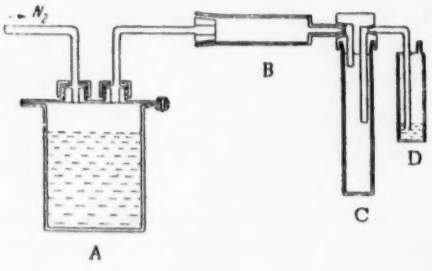
Rhenium hexafluoride, ReF_6, was first prepared by Ruff and Kwasnik [1] by the action of fluorine on metallic rhenium at 125°. In order to avoid the formation of rhenium oxyfluoride, the fluorine should not contain oxygen; removal of oxygen from gaseous fluorine was accomplished by means of a silent discharge (which results in the formation of fluorine oxide, F_2O_2). The rhenium hexafluoride obtained by this method apparently still contained a certain amount of fluorine oxides. A second report of the preparation of rhenium hexafluoride by this method was made in 1950. In this work, the fluorine was not freed of oxygen, but the resulting product was distilled in a stream of nitrogen for the recovery of pure ReF_6 [2].

The basic difficulty in all preparations of rhenium hexafluoride is the ease with which oxyfluorides are formed, which results in contamination of the product (a similar phenomenon has been observed during the fluorination of molybdenum) [3]. The formation of oxyfluorides is still more characteristic of rhenium, since it can be oxidized to the heptavalent state. As a consequence, the action of fluorine on oxygen-containing derivatives of rhenium forms oxyfluorides, but not ReF_6.

The action of the halogen fluorides BrF_3 [4] and IF_5 [5] on perrhenates leads to the formation of complex oxyfluorides of the type $ME^I[ReO_2F_4]$ in the first case and to perrhenyl fluoride, ReO_3F, in the second. Rhenium hexafluoride is not formed during these reactions. It was of interest to investigate chlorine trifluoride in similar reactions, since it is the most active fluorinating agent of all the halogen fluorides. We have previously established that metallic platinum is easily fluorinated by chlorine trifluoride to the tetravalent state [6]. This suggested the possibility of using this halogen fluoride for the fluorination of metallic rhenium. It was found that liquid ClF_3 has no effect on powdered rhenium, while with gaseous chlorine trifluoride, a reaction takes place at 300° which forms rhenium hexafluoride in good yield. The apparatus used in the experiments is shown schematically in Fig. 1. It consisted of a steel container A containing the chlorine trifluoride, a teflon reactor B containing the powdered rhenium, and a teflon receiver C, which was cooled with liquid nitrogen. The powdered rhenium was heated in a stream of hydrogen prior to the reaction. In order to prevent entrance of atmospheric moisture into the apparatus, the exit tube of the receiver was connected to a polyethylene Drechsel bottle D containing CCl_4.

At the beginning of an experiment, container A was cooled with dry ice, and a stream of nitrogen was then passed through it at a rate such that the bubbles rising in the Drechsel bottle G were individually discernable. The nitrogen had previously been dried with sulfuric acid, and was freed from oxygen with copper and given a final drying by passage through a coil immersed in liquid nitrogen. After all of the air had been purged from the system with nitrogen, the reactor heater was switched on. Simultaneously, container A was also warmed to 0°. The reaction proceeded at a temperature of 300°, and 12 g of rhenium reacted in 6 hours. The product collected in the receiver was a volatile yellow liquid containing ReF_6 and excess ClF_3. An attempt was made to recover pure ReF_6

by crystallization from liquid hydrogen fluoride. With this aim, the product in the receiver was dissolved in hydrogen fluoride, and the solution was cooled with dry ice. The mixture was allowed to stand, and coarse, light yellow crystals separated over a period of 8-10 hours. The remaining liquid contained almost no rhenium. The resulting crystals were recrystallized from hydrogen fluoride. The yellow crystalline material which precipitated when the HF solution was cooled was apparently a solvate, $ReF_6 \cdot xClF_3$, since it contained chlorine trifluoride. It melted at about 0°, and even in the liquid form it was only sparingly soluble in hydrogen fluoride. With the aim of obtaining pure ReF_6, the product was decomposed by distillation in a platinum tube at 50° under a stream of hydrogen. The resulting ReF_6 contained chlorine and hydrogen fluoride, from which it was purified by holding it under vacuum at −70° for 4 hours. Under the microscope, the pure rhenium hexafluoride appeared as coarse yellow crystals. The microscopic observations were carried out using a teflon cell in which the substance was sealed between two teflon films having a thickness of 0.05 mm. The product was identified by its melting point by chemical analysis. The capillary used in determining the melting point was made of thin teflon. The melting point of the ReF_6 was +18.7 ± 0.1°. The literature reports melting points of +18.8° [1] and +19° [2].



The operation of sampling the ReF_6 for analysis was carried out in a dry box. The weighed sample was hydrolyzed in a weighed quartz flask, in which had previously been placed an excess of KOH solution of known titer; the solution was frozed by immersing the flask in liquid nitrogen. When cooled in this manner, ReF_6 does not react with ice. The tightly sealed flask containing the sample and the alkaline solution was warmed to room temperature and weighed. A neutral solution of H_2O_2 was then added to the hydrosylate, and the contents of the flask were boiled for 3 minutes with protection from absorption of CO_2 from the atmosphere. The solution was cooled, and the excess base was titrated with hydrochloric acid. After hydrolysis and oxidation of 1 g of ReF_6, neutralization of the solution requires 0.233 equivalent of the base, in accordance with the equation $2ReF_6 + 14KOH + H_2O_2 = 2KReO_4 + 12KF + 8H_2O$. Experimentally, 1 g of the ReF_6 prepared as above required 0.234 equivalent. Aliquot portions of the solution were used in the determination of rhenium, as nitron perrhenate, and fluorine, by titration with $AlCl_3$ solution by the method of Kurtenacker and Jurenka [7].

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ON THE MECHANISM OF ISOTOPE EXCHANGE BETWEEN DIALKYLMERCURY COMPOUNDS AND ALKYLMERCURY HALIDES

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The present article describes a new isotope exchange reaction of alkylmercury compounds:

$$R_2Hg + RHg^{203}X \rightleftarrows R_2Hg^{203} + RHgX,$$

$$(R = (CH_3)_2CHCH_2CH_2\overset{*}{C}HCH_3,\ X = Br)$$

Optically active 5-bromomercuri-2-methylhexane and bis (2-methyl-5-hexyl) mercury [1] were used as starting materials.

The exchange was carried out in absolute alcohol at 60° in the dark using equimolar concentrations of the reactants (0.05 M). Samples of the reaction mixture (10-12 ml) were diluted with petroleum ether and washed several times with water for removal of the alcohol. The mixture of reagents in petroleum ether was resolved in an Al_2O_3 column. The dialkylmercury was eluted with petroleum ether, and the alkylmercury compound was eluted with ether.

The dialkylmercury was converted to the alkylmercury bromide by the action of $HgBr_2$. The radioactivity and, at the same time, the specific rotation of the latter compound were determined. The angle of rotation did not change during separation and purification of the substances.

Optically active alkylmercury bromide labeled with Hg^{203} and racemic dialkylmercury were used in Experiment No. 1. Redistribution of optical activity between RHgBr and R_2Hg occurred during the course of the reaction. The optical activity of the dialkylmercury (α_{R_2Hg}) was characterized through the use of twice the angle of rotation of the RHgBr obtained from the R_2Hg by the action of $HgBr_2$** (for RHgBr, $[\alpha]_D^{20} = \alpha_{RHgBr}$, $\alpha_{R_2Hg} = 2\alpha_{RHgBr}$).

All rotation measurements were carried out in absolute alcohol. Racemic RHgBr and optically active dialkylmercury with a specific rotation of $[\alpha]_D^{20} = -21.7°$ ($\alpha_{R_2Hg} = -31.4°$) were used in Experiment No. 2. The amount of optically active radicals in the reaction mixture was controlled by determining α_{RHgBr} and α_{R_2Hg} for the RHgBr and R_2Hg separated from each sample. In both the first and second experiments, the sum $\alpha_{RHgBr} + \alpha_{R_2Hg}$ remained constant from the beginning to the end of the reaction (within the limits of experimental error, ± 4%).

In Experiment No. 2, the angle of rotation of the reaction mixture increased with time, since active radicals were transferred from the dialkylmercury to the alkylmercury bromide, which has a higher specific rotation. These

* Deceased.

** The reaction of AlK_2Hg proceeds with complete retention of configuration at the asymmetric carbon atom [2,3].

data were used to calculate α_{R_2Hg} and $(\alpha_{RHgB_2} + \alpha_{R_2Hg})$, which were in good agreement with the values obtained after resolution of the mixture.

The results of the experiments are presented in Tables 1 and 2.

From the data presented in Tables 1 and 2 it follows, first of all, that the isotope exchange reaction takes place with strict retention of configuration at the asymmetric carbon atom: the sum $\alpha_{RHgBr} + \alpha_{R_2Hg}$ remained constant during the course of the reaction.

TABLE 1

Experiment No. 1*. Data on Isotope Exchange and Radical Exchange

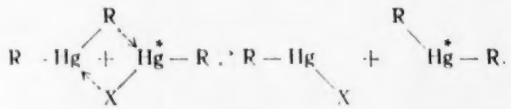
Time hr	Isotope exchange, %	α_{R_2Hg}	α_{RHgBr}	$\alpha_{RHgBr} + \alpha_{R_2Hg}$	Average sum $\alpha_{RHgBr} + \alpha_{R_2Hg}$
3	60,0	−7,6±0,5**	−15,4±0,3	−23,0±0,8	
5	70,0	−8,3±1,2	−12,2±0,2	−20,5±1,4	21,6±0,9
10	97,0	−10,6±0,2	−10,6±0,2	21,2±0,4	

*The reagents were dissolved together by heating; therefore, the initial rate was increased.

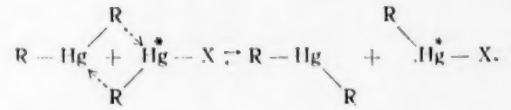
**The accuracy calculated from the calculated error in the measurements was ±0.005°.

We shall now consider possible mechanisms of the reaction:

I. Exchange of R and X (R⇌X).



II. Exchange of R and R (R⇌R).



III. Exchange of Hg and Hg^* (Hg⇌Hg).*

TABLE 2

Time, hr	α_{RHgBr}	α_{R_2Hg}	$\alpha_{RHgBr} + \alpha_{R_2Hg}$	Angle of rot. of mixture	Radical exchange, %	ln (1 − F)	$V \cdot 10^3$ moles/liter·hour	$V \cdot 10^3$, ave.
2	−3,2±0,2	−28,8±0,2	−32,0±0,4		21,2	0,103	4,0	
3	−3,1±0,2	−27,6±0,4	−30,7±0,6		32,7	0,172	4,4	
4	−3,9±0,3	−26,6±0,4	−30,5±0,7 −30,6*	−0,452	42,4	0,240	4,6	4,4±0,3
5	—	−25,8±0,4	—	—	50,0	0,301	4,6	
6	−4,8±0,3	−24,8±0,4	−29,6±0,7 −30,4*	−0,459	59,6	0,394	5,0	
15**	−10,8*	−20,2±0,5	−31,0*	−0,479	104			

*The angle was calculated from the angle of rotation of the reaction mixture.

**The mixture was held at room temperature for an additional 14 hours.

In this case, the two radicals in the R_2Hg "slide", so to speak, from their mercury atom to the radioactive mercury atom, and the R and X simultaneously "slide" from the radioactive mercury atom to the mercury atom which previously belonged to the R_2Hg molecule.

IV. A free-radical chain mechanism.

V. Isotope exchange complicated by the presence of the equilibrium:

$$2RHgX \rightleftarrows R_2Hg + HgX_2$$

Scheme 1 is in agreement with our experimental results; Schemes II-V contradict them.

TABLE 3

Experiment No. 2. Increase in Isotope Exchange

	Time, hours				
	2	3	4	5	6
Isotope exchange, %	33,0	48,5	54,0	65,0	69,5
$-\ln(1-F)$	0,174	0,287	0,338	0,426	0,516
$V \cdot 10^3$, mol/liter·hr	5,00	5,50	4,85	4,90	4,95
$V \cdot 10^3$, ave.		$5,0 \pm 0,2$			

Free radicals do not take part in the reaction as kinetically independent particles (Scheme IV), since there was complete retention of stereochemical configuration. Had the reaction proceeded according to Scheme III, there would have been no redistribution of optical activity between RHgX and R_2Hg.

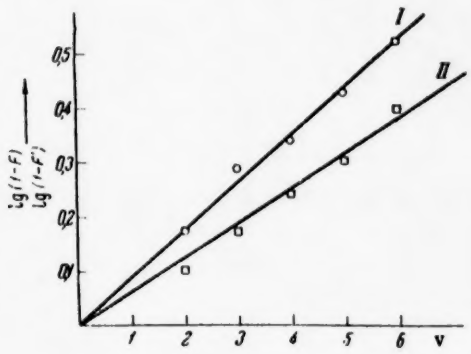


Fig. 1.

Considerations discussed below show that the isotope exchange was not complicated either by Equilibrium (a), Scheme V, or by parallel occurrence of reactions according to Scheme II and III.

The isotope exchange obeyed the equation:

$$-\ln(1-F) = \frac{A+B}{AB} Vt, \qquad (1)$$

where F is the degree of exchange, A and B are the concentrations of the original substances, V is the exchange rate constant, and t is time.

The redistribution of optically active radicals in the reaction:

$$R_2Hg + R^*HgBr \rightleftarrows RHgR^* + RHgBr,$$

where R* is the optically active radical, is, to a certain extent, analogous to isotope exchange. Since the radicals are chemically indistinguishable at any specific time, an equilibrium is established such that 1/3 of the initial amount of optically active radicals is in the RHgBr and 2/3 is in the dialkylmercury; after establishment of the equilibrium, redistribution proceeds at the same rate but, nevertheless, under conditions of "optical equilibrium".

Therefore, for the radical exchange process it is also possible to write an equation expressing the exponential dependence of degree of exchange on time:

$$-\ln(1-F') = \frac{2A+B}{2AB} V't, \qquad (2)$$

where F' is the degree of exchange of radicals ($F' = \frac{\alpha_t}{\alpha_\infty}$; α_t is the rotation of RHgX in time t, and α_∞ is the rotation of RHgX after establishment of equilibrium), A is the concentration of R_2Hg (it is doubled, since there are two radicals), B is the concentration of RHgX, V' is the rate constant, and t is time.

The experimentally obtained relationship between the degree of exchange of optically active radicals and time (Experiment No. 2) is shown in Fig. 1, II.

The increase in the degree of isotope exchange is shown on this same graph (Line I) and in Table 3.

It is evident that in accordance with Scheme I the exchange of mercury and radicals must proceed as a single act:

$$R^*Hg^{203}X + RHgR \rightleftarrows \dot{R}Hg^{203}R + RHgX$$
$$\dot{R}HgR + RHg^{203}X \rightleftarrows R_2Hg^{203} + \dot{R}HgX,$$

therefore, the rates of exchange, V and V', from Equations (1) and (2) can be equated: $V = V'$. If it is considered that the reaction occurs not only as a result of exchange of R and X, but also (though only partially) as a result of exchange of R and R (Scheme II), then the rate of radical exchange must exceed the rate of isotope exchange of mercury atoms ($V' > V$). If the sliding mechanism (Scheme III) played a role in the reaction, then V' would be less than V.

TABLE 4

Comparison of the Measured Angles of Rotation with Those Calculated from Isotope Exchange

		Time, hr						
		3*	5*	2	3	4	5	6
Measured	α_{R_2Hg}	−7,6°	−8,11°	−28,8°	−27,6°	−26,6°	−25,8°	−24,8°
Calculated	α_{R_2Hg}	−7,6°	−8,3°	−28,3°	−27,0°	−26,4°	−25,6°	−24,9°
Rel. Dev.		0%	2,5%	1,8%	2,2%	0,8%	0,8%	0,4%

*Data from Experiment No. 1; remaining data from Experiment No. 2.

It is also extremely improbable that the reaction proceeded simultaneously by Schemes II and III with retention of equal rates for these different processes.

For reaction in accordance with Scheme V

$$2R^*Hg^{203}X \rightleftarrows \dot{R}_2Hg^{203} + Hg^{203}X_2,$$
$$R_2Hg + Hg^{203}X_2 \rightleftarrows RHgX + RHg^{203}X$$

each separate exchange of mercury atoms must be accompanied by exchange of two optically active radicals (i.e., $V' > V$):

$$2R^*Hg^{203}X + R_2Hg \rightleftarrows \dot{R}_2Hg^{203} + RHg^{203}X + RHgX.$$

Our experiments established that V and V' are equal (Tables 2 and 3) within the limits of experimental error. Thus, we have shown that the reaction proceeds only by Scheme 1. Keeping in mind that $V = V'$, it is possible to derive an equation relating the degree of isotope exchange F and the degree of radical exchange F'. Dividing (1) by (2), we obtain:

$$\ln(1 - F') = \frac{2A + B}{2(A + B)} \ln(1 - F). \qquad (3)$$

Table 4 presents the angles of rotation (α_{R_2Hg}) calculated from the degree of isotope exchange by means of Equation (3) (the deviations from the experimental values do not exceed 2.5%).

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INVESTIGATIONS IN THE FIELD OF BORON COMPOUNDS. NEW DERIVATIVES OF TRIALLYLBORINE

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The present work is a continuation of our investigations of the chemical properties of triallylborine [1] in which we studied the interaction of triallylborine with acetic acid, ethyl and allyl alcohols, acetic anhydride, bromine, and pyridine. The following triallylborine derivatives are known: the anhydride and the dimethyl and di-n-butyl esters of allylboronic acid, diallyl-n-butylaminoborine, and certain other compounds prepared by B. M. Mikhailov and F. B. Tutorskaya [2].

In the present work, triallylborine, prepared by a method previously developed by the present authors [3], was subjected to the action of alcohols, acids, and aldehydes. All of the reactions were highly exothermic.

The interaction of triallylborine with alcohols at 20° results in the formation of the corresponding diesters of allylboronic acid:

$$(C_3H_5)_3B + ROH \rightarrow C_3H_5B(OR)_2 + C_3H_6.$$

The propylene evolved during the course of the reaction was collected in a carbon tetrachloride solution of bromine; this resulted in the formation of 1,2-dibromopropane, the amount of which corresponded precisely to the propylene evolved. The reactions of propylene with n-propyl, n-amyl, and benzyl alcohols and with phenol were studied. These reactions of triallylborine were carried out with excess alcohol in order to ensure complete consumption of the former. Di-n-propyl allylboronate, di-amyl allylboronate, dibenzyl allylboronate, and diphenyl allylboronate were prepared and characterized.

The interaction of triallylborine with acids resulted in the formation of diallylacyloxyboron, and propylene was evolved:

$$(C_3H_5)_3B + RCOOH \rightarrow (C_3H_5)_2BOCOR + C_3H_6,$$

where $R = C_6H_5$; C_3H_7.

In addition to diallylbenzoyloxyboron, allyldibenzoyloxyboron was also obtained during the interaction of triallylborine with benzoic acid.

Triallylborine reacted with aldehydes with the formation of esters of allylboronic acid, propylene, and cyclohexadiene in accordance with the equation:

$$(C_3H_5)_3B + RCHO \rightarrow C_3H_5B(OCH_2R)_2 + C_6H_8 + C_3H_6,$$

where R = C_3H_7; C_6H_5.

Propyl diallylborinate was obtained from the reaction with propionaldehyde. The physiochemical properties of the organoboron compounds synthesized are shown in Table 1.

Experimental

All experiments were carried out at 20° under argon which had been carefully freed of oxygen.

1. Di-n-propyl allylboronate. To 3.8 g of n-propyl alcohol was added dropwise 4.3 g of triallylborine. The gas evolved was collected in a solution of bromine in CCl_4, which was rapidly decolorized. The resulting solution was washed with a solution of soda and with water to a neutral reaction, and was dried over calcined $CaCl_2$. 1,2-Dibromopropane, b. p. 140.2°, was separated by distillation; $n^{20}D$ 1.5327 (literature: b.p. 141.6°; $n^{20}D$ 1.5367).

Distillation of the material in the reaction flask yielded a transparent, colorless liquid which boiled at 75-77°/35 mm; this was di-n-propyl allylboronate (yield, 87.5%), d^{20}_4 0.8657 n^{20}_D 1.4092.

	Found %:	C 64.1;	H 11.08; B 6.13
$C_3H_5B(OC_3H_7)_2$.	Calculated %:	C 63.5;	H 11.17; B 6.5

2. Di-n-amyl allylboronate. To 6.2 g of n-amyl alcohol was added dropwise 4.73 g of triallylborine. The reaction was strongly exothermic. Di-n-amyl allylboronate was separated from the reaction mixture by vacuum distillation (yield, 76%); this material was a transparent, colorless liquid with a b. p. of 132°/39 mm, d^{20}_4 0.8776; $n^{20}D$ 1.4223. The propylene evolved was collected in bromine solution.

	Found %:	C 69.9;	H 12.26; B 4.77
$C_3H_5B(OC_5H_{11})_2$.	Calculated %:	C 69.1;	H 11.94; B 4.8

3. Dibenzyl allylboronate. To 8.79 g of benzyl alcohol was added dropwise 5.45 g of triallylborine. Dibenzyl allylboronate, a colorless liquid boiling at 143-145°/3 mm, was obtained by fractional distillation of the reaction mixture (yield 76.4%); d^{20}_4 1.0663; $n^{20}D$ 1.5368. Propylene was evolved during the reaction, and this was collected in a solution of bromine in CCl_4.

	Found %:	C 76.6;	H 7.13; B 4.13
$C_3H_5B(OC_7H_7)_2$.	Calculated %:	C 76.7;	H 7.15; B 4.12

4. Diphenyl allylboronate. To 7.44 g of phenol was added dropwise 5.3 g of triallylborine. The reaction mixture was then distilled under vacuum, and a transparent, colorless liquid was obtained; this material, which boiled at 135-137°/15 mm, was diphenyl allylboronate (yield, 48%); d^{20}_4 1.0573; $n^{20}D$ 1.5373. A dark yellow residue was also obtained, but was not investigated further. A considerable amount of propylene was evolved during the reaction.

	Found %:	C 75.19;	H 6.59; B 4.57
$C_3H_5B(OC_6H_5)_2$.	Calculated %:	C 75.6;	H 6.3; B 4.62

5. Interaction of triallylborine with benzoic acid. To 5.56 g of benzoic acid was added dropwise 6.1 g of triallylborine. The reaction was strongly exothermic. The reaction mixture was vacuum distilled, and two fractions were collected: a) 110-112°/6 mm, diallylbenzoyloxyboron (yield, 42.8%), and b) a fraction boiling at 130°/6 mm, allyldibenzoyloxyboron (yield, 23.9%). Both fractions formed white crystals. After the distillation, a light orange polymer remained in the reaction flask; this material oxidized and darkened when exposed to air.

	Found %:	C 72.71;	H 7.05; B 4.72
$(C_3H_5)_2BOCOC_6H_5$.	Calculated %:	C 77.89;	H 7.01; B 5.14
	Found %:	C 68.98;	H 5.7; B 4.19
$C_3H_5B(OCOC_6H_5)_2$.	Calculated %:	C 69.38;	H 5.1; B 3.74

6. Interaction of triallylborine with n-butyric acid. The interaction of 4 g of triallylborine and 2.7 g of n-butyric acid gave diallylpropionyloxyboron—a heavy, colorless liquid boiling at 46-48°/5 mm (yield, 66.2%); d^{20}_4 0.9679; $n^{20}D$ 1.4472. A small amount of a dark orange solid polymer remained in the reaction flask after distillation of the diallylpropionyloxyboron.

Found %: C 67.12; H 9.99; B 5.74

$(C_3H_5)_2BOCOC_3H_7$. Calculated %: C 66.66; H 9.44; B 6.11

TABLE 1

Physicochemical Properties of the Organoboron Compounds Synthesized

Expt. No.	Compound	B.p., °C/mm	M.p., °C	Yield, %	Mol. wt. calc.	Mol. wt. found	d_4^{20}	n_D^{20}
1	$C_3H_5B(OC_3H_7)_2$	75—77/35	—	87,5	170	168,8	0,8657	1,4092
2	$C_3H_5B(OC_5H_{11})_2$	132/39	—	76,0	226	224,6	0,8776	1,4223
3	$C_3H_5B(OC_7H_7)_2$	143—145/3	—	76,4	266	264,3	1,0663	1,5368
4	$C_3H_5B(OC_6H_5)_2$	135—137/15	—	48,0	238	235,3	1,0573	1,5373
5	$(C_3H_5)_2BOCOC_3H_5$	110—112/6	84	42,8	214	212,8	—	—
6	$C_3H_5B(OCOC_3H_5)_2$	130/6	92,3	23,9	294	292,4	—	—
7	$(C_3H_5)_2BOCOC_3H_7$	46—48/5	—	66,2	180	183,9	0,9679	1,4472
8	$(C_3H_5)_2BOC_3H_7$	91/4	—	86,2	152	152,3	0,8905	1,4372
9	$C_3H_5B(OC_4H_9)_2$	75—76/6	—	53,6	198	202,02	0,8966	1,4350

Expt. No.	Compound	Elemental composition, % calculated			found		
		C	H	B	C	H	B
1	$C_3H_5B(OC_3H_7)_2$	63,5	11,17	6,5	64,1	11,08	6,13
2	$C_3H_5B(OC_5H_{11})_2$	69,1	11,94	4,8	69,9	12,26	4,77
3	$C_3H_5B(OC_7H_7)_2$	76,7	7,15	4,12	76,6	7,13	4,13
4	$C_3H_5B(OC_6H_5)_2$	75,6	6,3	4,62	75,19	6,59	4,57
5	$(C_3H_5)_2BOCOC_3H_5$	72,89	7,01	5,14	72,71	7,05	4,72
6	$C_3H_5B(OCOC_3H_5)_2$	69,38	5,1	3,74	68,98	5,7	4,19
7	$(C_3H_5)_2BOCOC_3H_7$	66,66	9,44	6,11	67,12	9,99	5,74
8	$(C_3H_5)_2BOC_3H_7$	71,05	11,9	7,23	70,28	12,03	6,94
9	$C_3H_5B(OC_4H_9)_2$	62,12	11,62	5,55	62,84	10,87	5,99

7. Reaction of triallylborine with propionaldehyde. To 3.9 g of propionaldehyde was added dropwise 9 g of triallylborine. The reaction was exothermic. Cyclohexadiene, which was collected in a cold trap at 0°, and propylene, which was collected in a solution of bromine in CCl_4, were evolved. Distillation of the reaction mixture gave a heavy, colorless, oily liquid with a b. p. of 91°/4 mm; this was the propyl ester of diallylborinic acid (yield, 86.2%); d_4^{20} 0.8905; $n^{20}D$ 1.4372.

Found %: C 70.28; H 12.03; B 6.94

$(C_3H_5)_2BOC_3H_7$. Calculated %: C 71.05; H 11.9; B 7.23

8. Reaction of triallylborine with benzaldehyde. The interaction of 5.49 g of triallylborine and 8.7 g of benzaldehyde was exothermic and propylene, which decolorized a solution of bromine in CCl_4, was evolved. Cyclohexadiene was collected in a trap cooled to 0°. From the reaction product was separated dibenzyl allylboronate, which boiled at 154-156°/5 mm; d_4^{20} 1.0668; $n^{20}D$ 1.5368.

Found %: C 69.7; H 12.38; B 4.71

$C_3H_5B(OC_7H_7)_2$. Calculated %: C 69.1; H 11.94; B 4.8

9. Reaction of triallylborine with butyraldehyde. To 3.1 g of butyraldehyde was added dropwise 5.75 g of triallylborine. The reaction was exothermic, and cyclohexadiene and propylene were evolved. Vacuum fractionation of the reaction mixture gave a colorless, oily liquid boiling at 75-76°/6 mm; this was dibutyl allylboronate (yield, 53.6%); d_4^{20} 0.8966; $n^{20}D$ 1.4350.

Found %: C 62.84; H 10.87; B 5.99

$C_3H_5B(OC_4H_9)_2$. Calculated %: C 62.12; H 11.62; B 5.55

All of these esters of allylboronic acid were tested as monomers for the preparation of boron-containing polymers.

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THE FORMATION OF TANTALUM IODIDES AND OF TANTALUM FROM THE IODIDES

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The study of iodides and the properties of metals obtained by thermal dissociation of these iodides has both theoretical and practical significance.

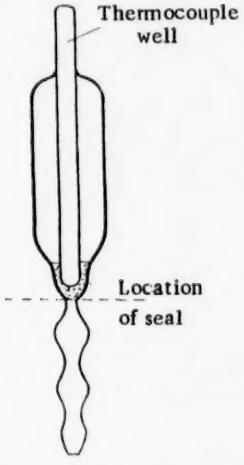

Fig. 1. Cell for thermographic study of the interaction of tantalum and iodine.

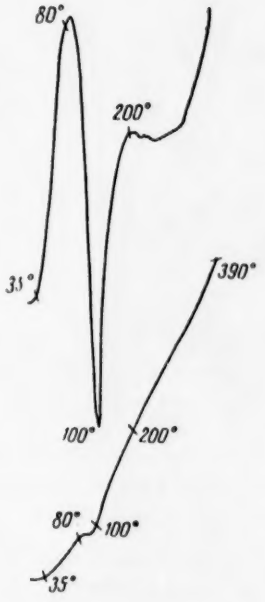

Fig. 2. Heating curve of a mixture of tantalum and iodine (to a temperature of 390°).

There is only a small amount of information in the literature relative to the synthesis of tantalum iodides from the elements and such information as exists is derived chiefly from the work of Rose [1], Moisson [2], Korösy [3], and Alexander and Fairbrother [4]. Both Rose and Moisson synthesized tantalum iodides at a temperature of 600°, while Korösy and Alexander and Fairbrother worked at temperatures of 1200-1500°.

The aims of the present work were to establish the temperature at which the interaction of tantalum and

iodine is initiated, to prepare tantalum iodides, and also to determine some of the properties of tantalum prepared by dissociation of its iodides. Tantalum having a purity of 97.8% and pure grade iodine were used for the synthesis of the tantalum iodides and the preparation of the metal from these iodides. These elements were subjected to additional purification. The tantalum was degassed by heating to a temperature of 400° for 3-4 hours, the gases being continuously removed by pumping at a residual pressure of 0.05-0.01 mm Hg. The iodine was purified by sublimation.

The tantalum iodide used in the preparation of tantalum was prepared by synthesis from the elements at 550°.

The mixture of tantalum and iodine, which contained a slight excess of iodine over the stoichiometric amount, was placed in a dry quartz tube, which was then pumped to 0.1-0.05 mm. The tube was sealed and placed in a furnace where it was maintained at a temperature of 550° for 3 hours. The temperature at which interaction of tantalum and iodine began was determined thermographically in a Kurnakov apparatus; the temperature was measured with platinum–platinorhodium differential thermocouples.

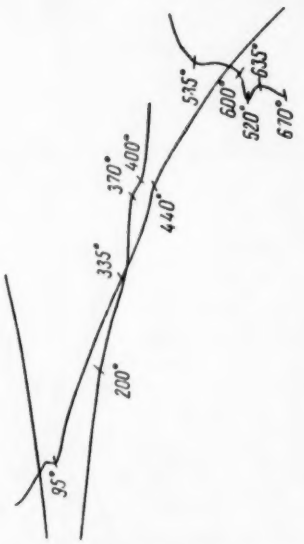

Fig. 3. Heating curve of a mixture of tantalum and iodine (up to a temperature of 670°).

The quartz cells (Fig. 1) had a wall thickness of 1-1.5 mm. One cell contained the mixture of tantalum and iodine, and the other contained calcined magnesium oxide, which was used as a standard for the differential temperature recording. The cells were evacuated to 10^{-2}–10^{-3} mm and then sealed. The heating rate was 8-10° per minute.

Figure 2 shows the heating curve; over the range 80-100-200° there is an endothermic effect which corresponds to melting and boiling of the iodine. Above 200-250°, the differential curve rises sharply, and stops abruptly at 390°; the tube exploded at this temperature.

A quartz tube with 3-mm walls was then constructed. The heating curve obtained with this cell is shown in Fig. 3. The first endothermic effect on this curve occurs in the same temperature range as in the first case (Fig. 2). There is a break in the simple thermocouple curve at a temperature of 370°; this corresponds to the beginning of interaction between the tantalum and iodine. The rate of the exothermic reaction was so high that it was impossible to obtain a trace on the photographic paper. At a temperature of about 400°, desorption of gases from the tantalum powder occurred; this was apparent from the sharp drop in the vacuum in the system when the tantalum was being evacuated. This temperature agrees with that for the initiation of the reaction between tantalum and iodine. It is apparent from the differential curve that interaction between tantalum and iodine proceeded with the liberation of considerable heat. The end of the exothermic effect is at 535°.

X-ray analysis of the products obtained as a result of the synthesis of tantalum iodides at a temperature of 530-550° showed the presence of a new substance. According to the chemical analysis of this material, the iodide had the formula $TaI_{2.8-3.0}$

From this thermographic study of the interaction of tantalum and iodine it follows that the reaction begins at 370-400° and proceeds very rapidly; under the experimental conditions used, the reaction is concluded at 535°. The resulting tantalum iodide undergoes a change which is characterized on the heating curve by an endothermic effect with a minimum at 620°.

In addition to the study of the reaction between tantalum and iodine, we also prepared threads of tantalum with a diameter of 0.7 mm by thermal dissociation of the tantalum iodides. The nature and quality of the deposits on the thread depended on the temperature of the iodide and thread, on the location of the iodide relative to the thread, and on the material of the core on which the deposition was carried out.

On a single-crystal tungsten thread, a deposit was obtained with a smooth surface and consisting of crystals oriented in one direction. The regular distribution of these crystals may be explained by automatic regulation of the rate of growth of the crystals (Fig. 4, 1). The ends of the threads consisted of fine crystals with disordered orientation, which was due to the lower temperature in these locations. On a polycrystalline tantalum thread,

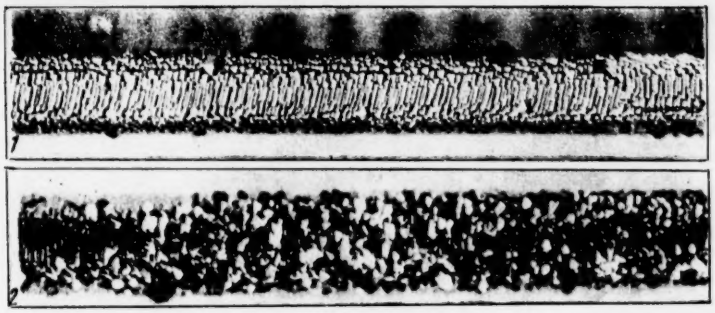

Fig. 4. Tantalum rods prepared from the iodide. 20×. 1) On tungsten core. 2) On tantalum core.

the deposit consisted of fine, variously oriented crystals (Fig. 4, 2).

According to spectroscopic analysis, the tantalum obtained by dissociation on an incandescent tantalum thread contained almost no gases or metallic impurities (iron, tin, lead); it possessed plastic properties, and could be formed at room temperature; the microhardness of the tantalum perpendicular to the cross section of the wire was 130-150 kg/sq mm at a load of 50 g.

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AUTOOXIDATION PRODUCTS OF Δ^3-CARENE

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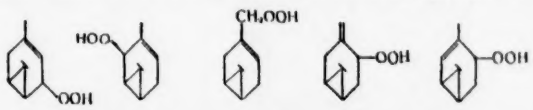
It is now generally known that the primary products of the autooxidation of unsaturated hydrocarbons are unsaturated hydroperoxides with an HOO group alpha to the double bond.

Autooxidation of unsaturated hydrocarbons, especially terpene hydrocarbons, is a complex process; the hydroperoxides formed undergo further conversions under the conditions of the oxidation–decomposition, interaction with the original hydrocarbons, isomerization, etc.

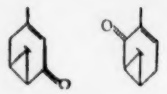
Among the terpene hydrocarbons, only α- and β-pinene have been sufficiently studied in this respect. The corresponding hydroperoxides, ketones, alcohols, oxides, and hydrocarbons have been identified in the oxidation products and in the products from reduction of the latter. Only a very small amount of work has been devoted to the autooxidation of Δ^3-carene. Owen and Simonsen [1] found by steam distillation of the reaction products that alcohols having the composition $C_{10}H_{16}O$ and ketones having the composition $C_{10}H_{14}O$ are formed in approximately equal amounts during autooxidation of Δ^3-carene with moist oxygen in the presence of cobalt resinate. However, the structures of these compounds were not established. Blohm and Widmark [2] have studied the kinetics of the autooxidation of Δ^3- carene.

In 1956, Erofeev and Chirko [3] prepared "Δ^3-carene hydroperoxide" by catalytic autooxidation of Δ^3-carene, and by reduction of this compound with potassium iodide in acetic acid they obtained an alcohol to which they ascribed the structure Δ^3-caren-2-ol, at the same time identifying it with the carenol obtained by Tishchenko [4] from 3-chloro-4-carene through the corresponding acetate and having the structure Δ^4-caren-3-ol. The sharp divergence of the data of Simonsen and of Erofeev and Chirko regarding the course of the autooxidation of Δ^3-carene merits attention; in the light of the literature data indicating the complexity of the autooxidation products of unsaturated hydrocarbons, such a clear-cut course of the oxidation of Δ^3-carene as obtained in the experiments of reference [3] seem remarkable.

Our present work began a study of the products of the autooxidation of Δ^3-carene when the oxidation is carried out in the presence of a catalyst (lead acetate, manganese dioxide). By analogy with the results of Bluman and Zeitschel [5], Suzuki [6], Schmidt [7], Schenck, Eggert and Denk [8], and Moore, Golumbic and Fischer [9] obtained by the autooxidation of α- and β-pinenes and with the data of Farmer, Koch and Sutton [10, 11] on double bond shifting accompanying the formation of unsaturated hydroperoxides, and, further, considering that the Δ^3-carene molecule has three "points of attack" in autooxidation reactions (two CH_2 groups and the CH_3 group in the alpha position to the double bond), it may be assumed a priori that the oxidation of Δ^3-carene with oxygen will not proceed in a clear-cut manner. The formation of the following hydroperoxides may be expected:



and reduction of these hydroperoxides may be expected to give the corresponding alcohols, the ketones



and hydrocarbons, products of the decomposition of the hydroperoxides. Even the first of our experiments confirmed this assumption of the complexity of the course of the autooxidation of Δ^3-carene.

The autooxidation of Δ^3-carene was carried out by passing oxygen into the hydrocarbon (while stirring vigorously to keep the catalyst in suspension) until the content of active oxygen in 1 ml of reaction mixture reached a constant value (0.1422-0.1465 g of hydroperoxide of the composition $C_{10}H_{16}O_2$ in 1 ml of reaction mixture).

Notwithstanding the results of Erofeev and Chirko, we were unable to isolate "Δ^3-carene hydroperoxide" in a pure form; upon distillation of the autooxidation products under high vacuum (0.025 mm), i.e., under the same conditions under which decomposition of the hydroperoxide did not occur in their experiments, the hydroperoxide content of the distillate was four times lower than in the undistilled products.

After removal of the unreacted Δ^3-carene, the reaction mixture from the autooxidation was reduced with sodium sulfite, and was fractionated in a column having an efficiency of 17 theoretical plates. The composition of the distillate was: 1) hydrocarbon fractions, $C_{10}H_{14}$, n^{20}_D 1.4940−1.5010; d^{20}_4 0.8338−0.8656 30%; 2) ketone fractions, n^{20}_D 1.4850−1.4929; d^{20}_4 0.9193−0.9380 29%; 3) alcohol fractions, n^{20}_D 1.4952−1.5039; d^{20}_4 0.9530 −0.9747 41%.

The I.R. spectrum of the ketone fraction had a band at 1656 cm^{-1}, which is characteristic of a C=O group conjugated with two double bonds. Crystalline derivatives melted as follows: semicarbazone, 182-184°; 2,4-dinitrophenylhydrazone, 149.5-150.5°. Hence, the ketone appeared to be identical to eucarvone (m. p.: semicarbazone, 183-185° [12], 2,4-dinitrophenylhydrazone, 152-153° [13]), a dienic hydrocarbon of the cycloheptane series, 2,6,6-trimethyl-2,4-cyclopentadien-1-one. The I.R. spectrum of eucarvone shows a corresponding band at 1660 cm^{-1} due to absorption of the C=O group.

The alcohol fractions of the products of the reduction of the Δ^3-carene autooxidation products contained both dextrorotatory and levorotatory alcohols of the composition $C_{10}H_{16}O$.

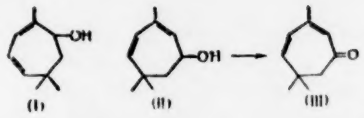
By treatment of the levorotatory alcohol (b. p., 62-64°/2 mm; n^{20}_D 1.4990, d^{20}_4 0.9754, α_D=−51.5°; MR found, 45.76; MR calculated for $C_{10}H_{16}O$ F one three-membered ring, 45.74) with p-nitrobenzoyl chloride, the p-nitrobenzoate was obtained, m. p. 154-155°. A mixed sample with known carenol p-nitrobenzoate (m. p., 155-156°; m. p. of the 3,5-dinitrobenzoate, 106-107°) prepared earlier by us [14] by reaction of Δ^3-carene oxide with acetic anhydride showed no depression of the melting point. Consequently, the alcohol obtained from the autooxidation of Δ^3-carene was identified as carenol; on the basis of an analysis of the I.R. spectra (the presence of bands characteristic of C=C and C−H valence vibrations, 1640 cm^{-1} and 890 cm^{-1}), we assign to this carenol the structure 4(7)-caren-3-ol:

The formation of the corresponding hydroperoxide was accompanied by shifting of the double bond, a phenomenon which has previously been observed during the photosensitized oxidation of α- and β-pinenes [8].

The dextrorotatory alcohol (b. p. 69-70°/1.5 mm; n^{20}_D 1.5026, d^{20}_4 0.9550, α_D=+55°; MR found, 47.01; MR calculated for $C_{10}H_{16}O$ F_2 46.77) formed a p-nitrobenzoate with an m. p. of 94-95.5° and a 3,5-dinitrobenzoate with an m. p. of 90.5-92°.

The infrared spectrum of this compound had absorption bands at 1593 cm^{-1} and 1639 cm^{-1}, which are characteristic of a conjugated double bond system. The presence of conjugated double bonds in the alcohol molecule was confirmed by Raman spectroscopy; frequencies of 1593 cm^{-1} [10], 1643 cm^{-1} [7], and 1658 cm^{-1} [7] were present. Phthalic acid titration indicated 1.5 double bonds. These data also indicate a monocyclic structure for the alcohol, specifically a cycloheptadiene structure.

The alcohol could have one of two possible structures:



(I) (II) (III)

2,6,6-trimethyl-2,4-cycloheptadien-1-ol (eucarveol) (I) or 3,6,6-trimethyl-2,4-heptadien-1-ol (II).

However, structure I may be excluded, since oxidation of the alcohol with chromium trioxide–pyridine complex gave a ketone with the following constants: m. p., 66-70°/3 mm; $n^{20}D$ 1.5098, d^{20}_4 0.9588; $\alpha_D = +84.5°$; these values are not in agreement with the properties of eucarvone. According to the melting point of the 2,4-dinitrophenylhydrazone (171-173°), the product of the oxidation of the alcohol was identical to the eucarvone isomer described by Campbell and Islam [13] (m. p. 2,4-dinitrophenylhydrazone, 172-173°), the structure of which was not determined by the authors.

The I.R. spectrum of the alcohol oxidation product had an absorption band at 1657 cm^{-1}, which is characteristic of a C=O group conjugated with two double bonds. The eucarvone isomer had a nearby band at 1668 cm^{-1} [13]. According to the authors of reference [13], the oxidation of the eucarvone isomer with $KMnO_4$ gives α,α-dimethylsuccinic acid, which also is in agreement with our proposed structures II and III for the alcohol and ketone, respectively.

The hydrocarbon fractions of the products of the autooxidation of Δ^3-carene were studied to a considerably lesser extent than were the other autooxidation products.

One of them, which had the composition $C_{10}H_{14}$, was purified by chromatographing on aluminum oxide (III, basic) and had the following constants: b. p., 52.5-54.5° /11.5 mm; $n^{20}D$ 1.4941; d^{20}_4 0.8656; $\alpha_D = +3.3°$; MR found 45.07; MR calculated for $C_{10}H_{14}F_2$, 43.74, exaltation 1.33. The infrared spectrum of this compound had absorption bands at 1640, 1603, and 890 cm^{-1}, which indicates the presence of a semicyclic double bond (see, for example, [15]). By analogy with the corresponding product of the autooxidation of α-pinene, verbenene [9], the structure 2,4(7)-caradiene may be assigned to this dienic hydrocarbon:

The possibility cannot be ignored that cycloheptatriene hydrocarbons were present in the hydrocarbon fractions. Terephthalic acid was not formed during oxidation of the hydrocarbon fractions with chromium trioxide; consequently, cymene was not present.

Thus, summarizing the above, it may be said that the Δ^3-carene molecule has three "points of attack": the CH_3 group and the two CH_2 groups alpha to the double bond; this is confirmed by the structures of the products isolated: 4(7)-caren-3-ol, eucarvone, and 3,6,6-trimethyl-2,4-cycloheptadien-1-ol. The formation of these products was accompanied by isomerization: a shift of the double bond from an endo to a semicyclic position or expansion of the six-membered ring to a seven-membered ring. It is also possible that during the autooxidation reaction there were formed the ketone 3,6,6-trimethyl-2,4-cycloheptadien-1-one (an isomer of eucarvone) and the alcohol corresponding to eucarvone, 2,6,6-trimethyl-2,4-cycloheptadien-1-ol, neither of which have we isolated yet.

This study of the composition and structures of the products of the autooxidation of Δ^3-carene is being continued.

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SYNTHESIS OF UNSATURATED ALKOXY, ARALKOXY, AND ALKYLMERCAPTO ACETALS AND UNSATURATED MERCAPTALS

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The synthesis of various unsaturated triethers, mercapto acetals, and dimercaptals is of interest in chemical synthesis, since it can serve as one of the major stages in the process of building up the carbon atom chain in molecules containing alkoxy and alkylmercapto groups. One method for the synthesis of such compounds is the interaction of ethynylvinyl ethers and thioethers, which may be obtained by reaction of diacetylene [1,2] with carbonyl compounds. A study of the reaction of ethyl orthoformate with certain vinyl ethers [3] and substituted vinyl ethers has led to the development of a general method for the synthesis of the tetraethyl acetals of different β-dicarbonyl compounds [4].

There is no description in the literature of this reaction with ethynylvinyl thioethers. The only ethynylvinyl ether which has been used in this reaction is ethynylvinyl methyl ether, to which ethyl orthoformate has been added by Grignard reaction [5]. The present paper reports the synthesis of alkoxy acetals and alkylmercapto acetals containing a pentenyne carbon atom chain with a conjugated multiple bond system; an interesting reaction in which alkoxy groups are replaced by alkylmercapto groups in these compounds is also reported. The synthesis of the unsaturated triethers and mercapto acetals was carried out according to the following scheme:

$$CH\equiv C-CH=CH-XR \xrightarrow{RMgBr} Br\,MgC\equiv C-CH=CH-XR \xrightarrow{CH(OC_2H_5)_3}$$

$$\rightarrow (C_2H_5O)_2CH-C\equiv C-CH=CH-XR$$

$RX = C_4H_9O$ (Ia); $C_6H_5CH_2O$ (Ib); $C_6H_5CH_2CH_2O$ (Ic); $RX = C_2H_5S$ (IIa); C_4H_9S (IIb)

This method led to good yields of the final products, which contained alkyl and aralkyl radicals. Inasmuch as the resulting sulfur-containing acetals have not been investigated, it seemed desirable to study their properties, particularly the addition of mercaptans to them, which would be expected to result in the formation of mixed mercapto acetals. However, in the interaction of mercapto acetals with ethyl mercaptan, the chief product proved to be 1,5-bis(diethylmercapto)-3-pentyne (III), which was formed as a consequence of the exchange of alkoxy groups for alkylmercapto groups and the addition of a molecule of mercaptan across the double bond of the original mercapto acetal and subsequent disproportionation:

$$\left.\begin{matrix} R'S-CH=CH-C\equiv C-CH(OC_2H_5)_2 \\ R''O-CH=CH-C\equiv C-CH(OC_2H_5)_2 \end{matrix}\right\} \xrightarrow{4RSH} \underset{RS}{\overset{RS}{\rangle}}CH-\underset{(III)}{CH_2-C\equiv C-CH}\langle^{SR}_{SR} + 4R''OH$$

$R' = R = C_2H_5$ (IIIa); $R'' = C_4H_9$; $R = C_2H_5$ (IIIb)

It is well known [6-9] that the alkoxy groups in acetals are labile; however, the literature contains no indication that they can be replaced by alkylmercapto radicals by interaction with mercaptans. Therefore, it was of interest to determine whether this reaction is a characteristic of the above acetals or is general. For this reason, we studied the reaction of various acetals of acetaldehyde, 3-butoxybutanal, and tetrolic aldehyde [2-butynal] with ethyl mercaptan.

In all cases, reaction occurred with exchange of alkoxy and aralkoxy groups of the acetal for the alkylmercapto radical of the mercaptan, which resulted in the formation of the corresponding mercaptals:

$$CH_3 - CH(OR)_2 + 2C_2H_5SH \rightarrow CH_3 - CH(SC_2H_5)_2, \quad (IV)$$

$$R = C_2H_5 \ (IV\,a); \quad C_4H_9 \ (IV\,b);$$

$$CH_3 - CH(OC_4H_9) - CH_2 - CH(OC_4H_9)_2 + 2C_2H_5SH \rightarrow$$

$$\rightarrow CH_3 - CH(OC_4H_9) - CH_2 - CH(SC_2H_5)_2, \quad (V)$$

$$CH_3 - C \equiv C - CH(OCH_2C_6H_5)_2 + 2C_2H_5SH \rightarrow CH_3 - C \equiv C - CH(SC_2H_5)_2; \quad (VI)$$

which indicates that the above reaction is general.

It is known [10] that the synthesis of the mercaptal of acetaldehyde from ethyl vinyl sulfide and ethyl mercaptan is complicated by a concurrent reaction in which the mercaptan is added contrary to Markovnikov's rule, as a result of which the yield of mercaptan is very low. The side reaction is not completely suppressed even in the presence of SO_2 and with maximum elimination of atmospheric oxygen. The synthesis of mercaptals from acetylene and mercaptans in the presence of CuCl [11] does not give yields of mercaptals greater than 50%.

The structure of the mercaptals synthesized was demonstrated by reaction with an alcoholic solution of mercuric chloride [2, 10].

1. Synthesis of triethers and mercapto acetals. The diethyl acetal of 5-benzoxypenten-4-yne-2-al (Ib) was prepared (in a flask fitted with a stirrer and thermometer) from the organomagnesium complex (1.0 g of Mg and 4.7 g of C_2H_5Br) in ether and 4.5 g (0.02 mole) of benzyl ethynylvinyl ether. The ether was added at −10°, and 6.1 g of ethyl orthoformate was subsequently added at a temperature not exceeding 25°. The reaction mixture was treated with an aqueous solution of ammonium chloride, and the ether layer was then dried with sodium sulfate and distilled under vacuum. The distillation resulted in 5.6 g of a fraction boiling at 108-110° (0.007 mm), which, after a second distillation, had the constants shown in Table 1 for the diethyl acetal of benzoxypentenynal.

In a similar manner was synthesized the diethyl acetal of 5-butoxy- and 5-phenylethoxypentenynal (Ia and Ic), the constants and yields of which are shown in Table 1.

The diethyl acetals of 5-ethylmercapto- and 5-butylmercaptopentenynals (IIa and IIb) were synthesized from ethynylvinyl ethyl and ethynylvinyl butyl sulfides under conditions similar to those described above. The constants of these compounds are shown in Table 1.

2. Synthesis of the bisdiethylmercaptal of 3-pentyne-1,5-dial (III). A sealed tube containing 8.3 g (0.04 mole) of the diethylmercaptal of 5-ethylmercaptopentenynal (IIa) and 14.9 g (0.24 mole) of ethyl mercaptan was heated on an oil bath at 115-120° for 16 hours. Distillation yielded 4.6 g of a fraction boiling at 130-132° (0.01 mm), which, after a second distillation, had the constants shown in Table 1 for the bisdiethylmercaptal of 3-pentyne-1,5-dial (IIIa). The results of mercuric chloride titration of the fraction boiling at 120-122° (0.008 mm) (IIIa) are also shown in the table; the bisdiethylmercaptal of 3-pentyne-1,5-dial (IIIa) was prepared in a similar manner from the diethyl acetal of 5-butoxypentenynal (IIIb); the yield was 50% of theoretical. The material boiled at 123-125° (0.01 mm); n^{20}_D 1.6030.

3. Synthesis of a diethylmercaptal from an acetal of acetaldehyde (IV). 1) A mixture of 8 g (0.045 mole) of acetaldehyde dibutyl acetal and 12.4 g (0.18 mole) of ethyl mercaptan was heated in a tube on a boiling water bath for 16 hours. Vacuum distillation gave 5.8 g (84.2%) of acetaldehyde diethylmercaptal, which, after a second distillation (yield, 5.1 g), had the constants shown in Table 1.

2) In a similar manner, but with a heating time of 6 hours, from 5.9 g of acetal and 12.4 g of ethyl mercaptan was obtained 5.7 g (76.5%) of acetaldehyde diethylmercaptal fraction boiling at 80-82° (21 mm), n^{20}_D 1.5010. This fraction had a diethylmercaptal content of 94.63%, according to mercuric chloride titration.

4. Synthesis of the diethylmercaptal of 3-butoxybutanal (V). Heating for 16 hours of a mixture of 5.5 g (0.02 mole) of 3-butoxybutanal dibutyl acetal [6] and 5 g (0.08 mole) of ethyl mercaptan gave 4.5 g (90% of theoretical) of a fraction boiling at 123-127° (5 mm), which was shown to be the diethylmercaptal of 3-butoxybutanal. After a second distillation, this material had the constants shown in Table 1.

5. Synthesis of the diethylmercaptal of tetrolic aldehyde (VI). Heating of 2.6 g (0.012 mole) of tetrolic aldehyde dibenzyl acetal (I) and 3 g (0.05 mole) of ethyl mercaptan at 110-120° for 24 hours gave 1 g of a fraction boiling at 130-135° (4 mm), the diethylmercaptal of tetrolic aldehyde. After a second distillation, this material had the constants shown in Table 1.

The reaction of these mercaptals with an alcoholic solution of mercuric chloride and subsequent titration with HCl was carried out by the method described previously [2, 10]. The results of the titrations are shown in Table 1.

Thus, conditions have been found for the synthesis of triethers and mercapto acetals of the pentenyne series containing alkyl and aralkyl radicals. The reaction of acetals of various aldehydes with mercaptans has been studied. It has been shown that this reaction is a general one, and that it is a convenient method for the synthesis of a variety of mercaptals and bismercaptals from the corresponding acetals, triethers, and mercapto acetals. The addition of a mercaptan to the alkylmercaptovinyl end of the molecule, which leads to a mercaptal group, is indicative of the peculiarities of a double bond conjugated with a triple bond in triethers and mercapto acetals.

Compound	Yield, % of theor.	B.p., °C (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % S	Calculated, % C	Calculated, % H	Calculated, % S	Titration with $HgCl_2$: wt., g	Titration with $HgCl_2$: 0.1 N NaOH, ml	Titration with $HgCl_2$: % mercaptal
Ia $C_4H_9OCH{=}CH{-}C{\equiv}C{-}CH(OC_4H_9)_2$	70.0	133 (3)	1.4698	0.9422	66.99	64.63	69.00 68.92	9.64 9.56	—	68.99	9.78	—	—	—	—
Ib $C_6H_5CH_2OCH{=}CH{-}C{\equiv}C{-}CH(OC_6H_5)_2$	60.8	119.5—120(0.01)	1.5247	1.1242	70.90	69.69	73.96 73.64	7.90 7.72	—	73.82	7.74	—	—	—	—
Ic $C_6H_5CH_2CH_2OCH{=}CH{-}C{\equiv}C{-}CH(OC_6H_5)_2$	45.3	112 (0.007)	1.5223	1.0202	82.06	79.50	74.05 74.09	8.19 8.10	— 14.85	74.42	8.08	—	—	—	—
IIa $C_4H_9SCH{=}CH{-}C{\equiv}C{-}CH(OC_4H_9)_2$	58.8	127 (4)	1.5125	0.9908	64.96	61.72	61.67 61.85	8.77 8.35	14.95 13.23	61.64	8.46	14.96	—	—	—
IIb $C_6H_5SCH{=}CH{-}C{\equiv}C{-}CH(OC_6H_5)_2$	80.0	147 (4)	1.5045	0.9713	73.95	70.95	64.03 64.08	9.24 9.29	13.23 13.19	64.42	9.15	13.23	—	—	—
III. $(C_6H_5S)_2CH{-}CH_2{-}C{\equiv}C{-}CH(SC_2H_5)_2$	50—38.3	122 (0.008)	1.6035	1.0890	97.25	92.05	50.44 50.49	7.62 7.80	40.85 40.88	50.61	7.83	41.55	0.14915 0.04185	15.77 4.29	79.73 79.15
IV. $CH_3{-}CH(SC_2H_5)_2$	84.2	78.5 (16)	1.5022	0.9725	46.72	45.85	47.84 47.93	9.27 9.34	42.64 42.61	47.94	9.37	42.66	0.1912 0.2113	25.14 27.86	99.82 99.09
V. $CH_3{-}CH(OC_4H_9){-}CH_2{-}CH(SC_4H_9)_2$	90.0	123.5—124(4)	1.4832	0.9498	75.34	75.20	57.30 57.43	10.35 10.44	25.48 25.71	57.52	10.49	25.60	0.1891 0.1974	14.96 15.61	99.04 99.06
VI. $CH_3{-}C{\equiv}C{-}CH(SC_2H_5)_2$	50.0	128—130(3.5)	1.5479	1.0482	52.82	53.02									

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THE COMPOSITION AND STABILITY OF CALCIUM HYDROSILICATES UNDER HYDROTHERMAL TREATMENT AT 700 ATMOSPHERES (GAUGE) AND 200 DEGREES

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The temperature in very deep oil wells reaches 200°, and the pressure is as high as 700 atm (gauge). When the wells are cemented, the cement must harden under especially severe conditions. In a study of the effect of these conditions on the hardening of cement, we investigated the composition and degree of stability of calcium hydrosilicates obtained by synthesis from a mixture of lime and quartz sand at CaO to SiO_2 ratios of 2, 1, and 0.8 at a temperature of 200° and a pressure of 700 atm (gauge) and, for comparison, at a temperature of 200° and a pressure of 16 atm (gauge). The work was carried out at the Scientific Research Institute for Cement. Chemically pure calcium oxide and quartz sand washed and ground in a porcelain mill to S = 3500 sq cm/g (Tovarov's method) were used in the synthesis of the hydrosilicates.

These mixtures were mixed with distilled water to form a plastic mass, and the mass was then poured into forms 1 × 1 × 3 cm. Some of the samples in the forms were placed in a GROZNII autoclave system specially designed for high pressures, and the hardening process was carried out at 200° and 700 atm (gauge). The remainder of the samples were placed in an autoclave where synthesis proceeded at 200° and 16 atm (gauge). The time for which the samples were maintained under these temperature and pressure conditions was determined by the experimental conditions. The strength of the sample was determined at the end of the experiment.

The phase composition was established by x-ray, thermal, and petrographic methods. The x-ray patterns were obtained with a URS-501 diffraction apparatus, and the thermograms were obtained with a Kurnakov pyrometric apparatus. The x-ray and thermal characteristics of the synthesis products used for comparison with the properties determined in the present work were taken from references [1-4].

Hydrothermal treatment of the mixture having a CaO to SiO_2 ratio of 2 at both low and high pressure gave the hydrosilicate $C_2SH(C)$ (Table 1), which was identified on the x-ray patterns by lines with d = 5.43, 4.06, 3.82, 3.60, 3.34, 3.04, 2.91, 2.84, 2.70, 2.56, and 2.51 A and others. Its presence was also confirmed by endothermic effects at 680 and 730° on the DTA curves.

Under the microscope, the synthesis products appeared as an extremely fine-grained, almost isotropic mass (Fig. 3a). Free lime and unreacted quartz were not found in the samples. The resulting calcium hydrosilicates had practically no cementing properties. Treatment of a mixture having a CaO to SiO_2 ratio of 1 in the autoclave for three days led to the formation of a phase consisting almost entirely of xonotlite. Its formation proceeded through calcium hydrosilicates which are metastable under the given conditions and which were formed earlier in the process (Table 1, Figs. 1 and 2).

TABLE 1

Phase Composition, Optical Constants, and Strength of Samples Prepared from Mixtures of Lime and Quartz Sand

Expt. No.	Treatment conditions at 200°		Strength, kg/sq cm		N_{av}	Phase composition
	press., atm (gauge)	Time, hours	Bending	Compression		
			$CaO : SiO_2 = 2$			
1	16	72	0	0		$C_2SH(C)$; $C_2SH(B)$
2	16	120	0	0		The same
3	16	168	0	0		$C_2SH(C)$
4	700	72	0	0		The same
5	700	120	0	0		" "
6	700	168	0	0	1,630—1,635	" "
			$CaO : SiO_2 = 1$			
7	16	3	27	130		$C_2SH(C)$; $CSH(B)$; C : S=0,8, 1,25; $C_4S_3H_3$; $Ca(OH)_2$; SiO_2
8	16	24	34	122		$C_2SH(C)$; $CSH(B)$; C : S=0,8; $CSH_{0,18}$
9	16	72	29	125		$CSH_{0,18}$;
10	16	120	—	127		The same
11	16	168	26	124		" "
12	700	3	19	83		$C_2SH(C)$; $CSH(B)$; C : S=0,8; $C_4S_3H_3$; $Ca(OH)_2$; SiO_2
13	700	24	9	75		$CSH(B)$; C : S=0,8; $CSH_{0,18}$;
14	700	72	brittle	75		$CSH_{0,18}$
15	700	120	"	70		The same
16	700	168	"	75	1,579±0,003	" "
			$CaO : SiO_2 = 0,8$			
17	16	3	25	110		$C_4S_3H_3$; $CSH_{0,18}$; $CSH(B)$; C : S=1,25; SiO_2
18	16	24	—	85		$C_4S_3H_3$; $CSH_{0,18}$; $CSH(B)$; C : S=0,8; SiO_2
19	16	72	30	75		The same
20	16	120	35	92		" "
21	16	168	23	95		" "
22	700	3	21	105		" "
23	700	24	30	100		" "
24	700	72	22	130		" "
25	700	120	31	110		" "
26	700	168	24	120	1,564±0,003	" "

Hydrothermal treatment longer than three days produced no appreciable change in the phase composition. However, with an increase in the time in the autoclave, the bending strength of the samples decreased sharply; this can be explained by growth of the xonotlite crystals in a medium of superheated water at 700 atm (gauge).

There were small thermal effects at 755° (+) and 770° (−) on the DTA curves of samples consisting of xonotlite $CSH_{0,18}$ (Fig. 2, Curves 2, 3, and 5). The x-ray patterns had lines with d = 2.62, 1.676, 1.562, 1.514, 1.426, and 1.385 A, but we were unable to identify them.

The synthesis product obtained at a pressure of 700 atm (gauge) and a time of seven days was a finely crystalline mass with a comparatively homogeneous composition (Fig. 3b). The hydrosilicate was in the form of very fine, almost isotropic grains, which were partly cemented together to form granules having in their centers spherulites with high birefringence.

A one-day autoclave treatment of mixtures with a CaO to SiO_2 ratio of 0.8 gave a practically constant ratio of the hydrosilicates xonotlite, tobermorite, and fibrous CSH(B), the amount and crystallization of which did not change appreciably with an increase in the treatment time (Figs. 1 and 2, Curves 6-10). The strengths of these samples also underwent no substantial change with an increase in treatment time, which indicates retention of structure by the hardened conglomerate. The presence of tobermorite was confirmed by an endothermic effect at 230° on the DTA curves; the presence of the hydrosilicate CSH(B) C:S = 0.8 was determined from an exothermic effect at 845°.

The presence of unreacted quartz was detected by both x-ray and petrographic analysis.

Under the microscope, the synthesis products were characterized by an extremely finely crystalline structure consisting of minute grains, sometimes bound together with the formation of fine plates or granules. Moreover,

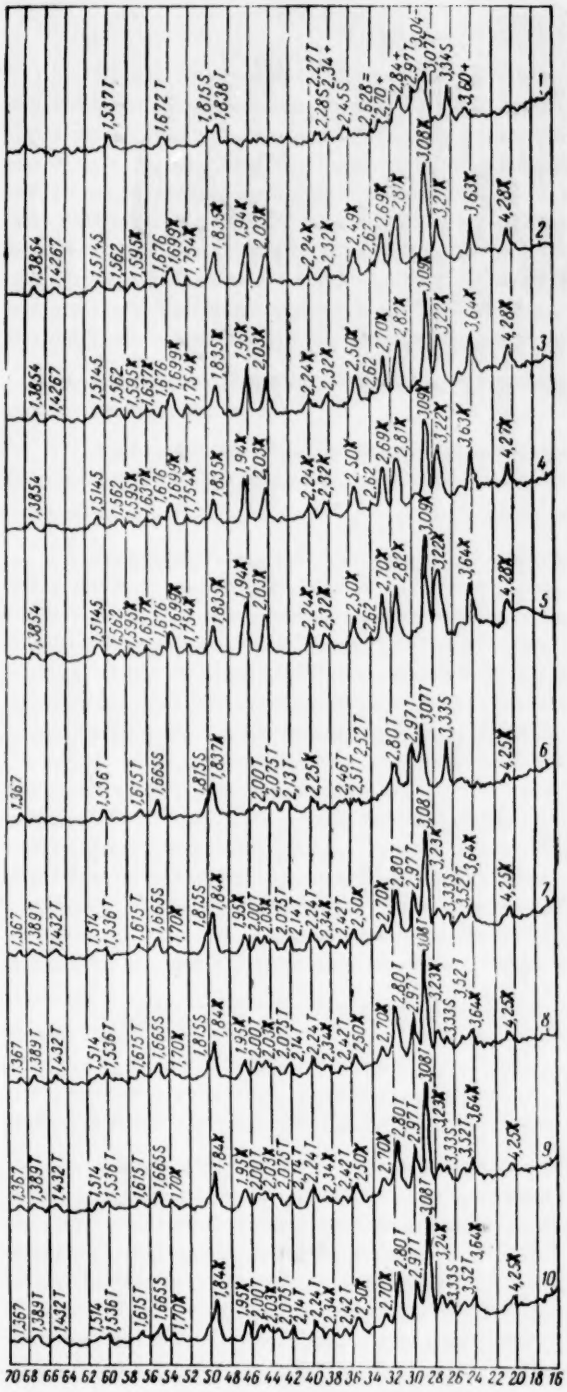

Fig. 1. X-ray curves of products of syntheses from lime and quartz sand with a CaO to SiO_2 ratio of 1 (Curves 1-5) and 0.8 (Curves 6-10); treatment at 200° and 700 atm (gauge) for: 3 hours, Curves 1 and 6; 1 day, Curves 2 and 7; 3 days, Curves 3 and 8; 5 days, Curves 4 and 9; 7 days, Curves 5 and 10.

all samples contained fine spherulitic formations, usually associated with xonotlite.

The synthesis process of calcium hydrosilicates occurring at 700 atm (gauge) and 200° differs qualitatively and quantitatively from the process occurring at 16 atm (gauge) and the same temperature. This is especially evident for the mixture with a CaO to SiO_2 ratio of 0.8; with a treatment time of 3 hours and a pressure of 700 atm (gauge), CSH(B) is formed with a C:S of 0.8, while at 16 atm (gauge), CSH(B) is formed with C:S of 1.25 (Fig. 2, Curve 6).

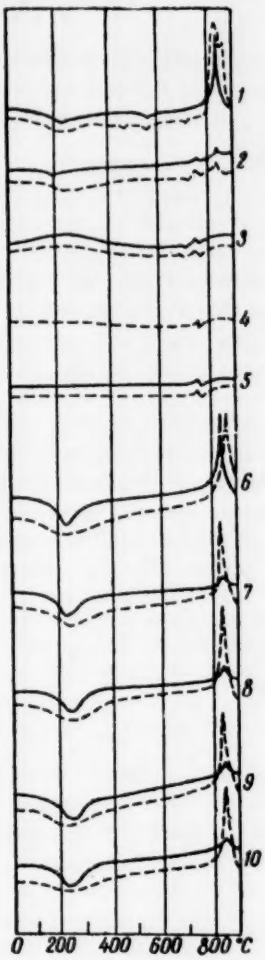

Fig. 2. Thermograms of synthesis products from lime and quartz sand. Legends for the curves are the same as in Fig. 1. Thermograms of samples synthesized at 16 atm (gauge) are indicated by broken lines.

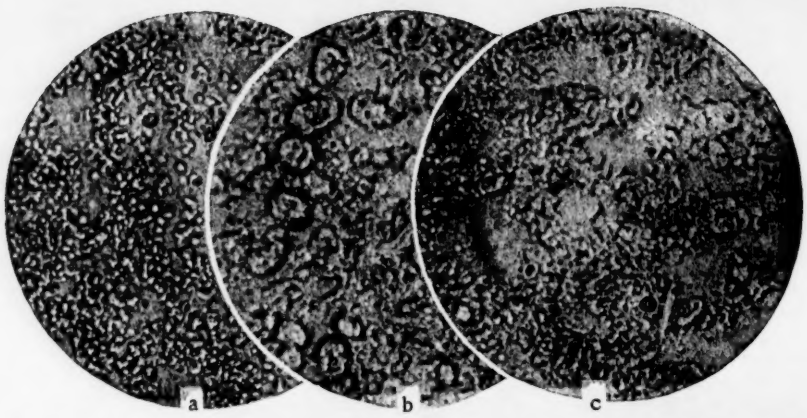

Fig. 3. Microstructure of calcium hydrosilicates prepared at 200°, 700 atm (gauge), and 7 days with an initial mixture ratio of: a) $CaO:SiO_2 = 2$; b) $CaO:SiO_2 = 1$; c) $CaO:SiO_2 = 0.8$. No analyzer. 600×.

In the ensuing treatment period, the amount of CSH(B) (exothermic effect at 845°) and tobermorite (endothermic effect at 230°) in the samples depended on the pressure (Fig. 2, Curves 7-10).

The x-ray patterns of samples prepared at 700 atm (gauge) were characterized by a greater number of lines of higher intensity, from which individual compounds were determined, than the x-ray patterns of samples treated for the same time at 16 atm (gauge).

The calcium hydrosilicates synthesized at 16 atm (gauge) were distinguished by finer crystals, less distinguishable minerals, and more homogeneous composition.

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ISOTOPE EXCHANGE OF NITROGEN IN AMIDES

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In our preceding communications [1, 2], we presented data from a systematic study of the exchange of nitrogen between liquid ammonia and amino compounds as a function of the structure of the latter. It was found that this exchange occurs only in compounds in which the carbon atom connected to the amino group acquires an electrophilic character by reason of the inductive action of the groups joined to it and conjugation with them. The rate of exchange increases with an increase in the positive charge on the carbon atom. On the basis of these data, an exchange mechanism was proposed, the essence of which was a nucleophilic attack of the nitrogen of the ammonia on the carbonyl carbon with transfer of a proton to the original amino group and splitting off of the latter. This mechanism is in agreement with the acceleration which we found to occur in the presence of NH_4Cl.

This same depence of the rate of exchange on the electrophilic nature of the carbonyl carbon was observed for several of the amides studied at that time. It was also observed by Heyns and co-workers [3] in work published shortly after ours. In this work, the exchange kinetics were determined quantitatively only for p-nitrobenzamide in the presence of NH_4Cl, since their experiments, in contrast to ours, were carried out at relatively low temperatures where for the majority of amides exchange proceeds only to the extent of a few percent of equilibrium in 3-7 days.

The study of the exchange of amino groups in amides is of particular interest owing to the similarity of this reaction to hydrolysis of amides and ammonolysis of esters, the mechanisms of which have been studied in previous work [4], which, however, did not lead to a final conclusion.

The present communication presents data on the effect of substituents and of the structure of the radical on the rate of exchange of the amino group in amides with ammonia, both with and without the addition of NH_4Cl as an acid catalyst.

The results of the kinetic measurements are presented in Table 1, where the values shown are average values for the first order rate constant and half-life periods. The amides $RCO{\cdot}NH_3$ may be arranged in the following series with respect to dependence of the rate of exchange on the radical R*:

$$CCl_3 > CHCl_2 > H > CH_2F > NH_2 > C_2H_5O > CH_3 \text{ and } X{-}C_6H_4.$$

The difference in rates in this series is very great: from a half-life of 12 minutes at 25° for trichloroacetamide to 3.6-17 hours at 180° for acetamide and the benzamides and no exchange at all in 20 hours at 180° for p-methylbenzamide. Para substituents in the benzamides have considerably less influence and may be arranged in the series:

$$NO_2 > OCH_3 > Br > H > Cl > CH_3.$$

* The data for $CCl_3CO{\cdot}NH_2$, NH_2CONH_2, $C_6H_5CONH_2$ and CH_3CONH_2 have been reported in reference [2].

A nitro group in the meta position accelerates exchange to a greater extent than it does in the para position, and a chlorine in the ortho position inhibits exchange to a greater extent than it does in the para position.

In the presence of NH_4^+, exchange is always accelerated, and, with slight rearrangement, the same order is retained in the series, but in substituted benzamides, the effect of substituents is more weakly expressed. Substituents in the para position of benzamide fall in the following series:

$$NO_2,\ Br > Cl > OCH_3 > H > CH_3.$$

A nitro group in the meta position more strongly accelerates exchange, and a chlorine or bromine in the ortho position considerably inhibits exchange.

TABLE 1

Rate Constants and Half-Life Periods for Exchange in Amides

Substance	Temp, °C	Moles amide per mole NH_3	k, hours $^{-1}$	Half-life, hours
Trichloroacetamide [2]	25	0.4-0.5	3.6	0.19
Same + NH_4Cl	25		complete in 2 min.	
Dichloroacetamide	22	0.6-0.7	0.493	1.41
Formamide	50	0.9-1.0	0.799	0.87
Fluoroacetamide	50	0.33	0.153	4.5
Acetamide [2]	180		0.13	5.3
		1.0		
Same + NH_4Cl	120		0.61	1.1
p-Nitrobenzamide	180		0.192	3.6
		0.2		
Same + NH_4Cl	180		1.51	0.46
m-Nitrobenzamide	180		0.118	5.9
		0.4		
Same + NH_4Cl	180		2.28	0.30
p-Bromobenzamide	180		0.096	7.3
		0.35		
Same + NH_4Cl	180		1.51	0.46
o-Bromobenzamide + + NH_4Cl	180	0.5	0.249	2.8
p-Chlorobenzamide	180		0.0418	16.6
		0.5		
Same + NH_4Cl	180		1.25	0.55
o-Chlorobenzamide	180		0.0317	22
		0.5		
Same + NH_4Cl	180		0.285	2.4
p-Methoxybenzamide	180		0.151	4.6
		0.5		
Same + NH_4Cl	180		0.13	0.61
Benzamide	180		0.059	11.8
Same + NH_4Cl	180	0.9-1.0	0.94	0.74
Same + NH_4Cl	160		0.069	10.0
p-Methylbenzamide	180		no exchange	
		0.9-1.0		
Same + NH_4Cl	180		0.685	1.02

A comparison of these data reveals that electron-donor radicals and substituents in the para and meta positions inhibit exchange, while acceptor radicals accelerate it in accordance with the accelerating action of a decrease in electron density at the carbon in the C-NH_2 bond, a general effect for amino compounds. This same

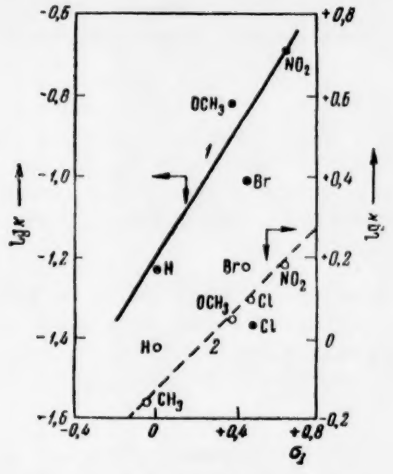

Fig. 1. Dependence of log $\underline{k}$ for para-substituted benzamides on the inductive component σ_i of the Hammett equation. 1) Exchange in NH_3 (left ordinate); 2) exchange in NH_3 + 1 N NH_4Cl.

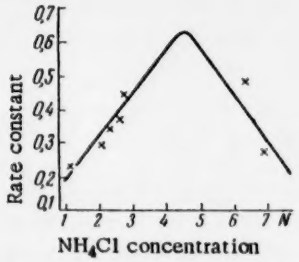

Fig. 2. Dependence of exchange rate for benzamide at 150° on concentration of NH_4Cl.

effect of substituents is known to hold for the rates of hydrolysis of esters [4, 5], hydrolysis of amides * [7-9], and ammonolysis of esters [6]. The small effect of the specific substituents in benzamide as compared to the effect of the nature of the radical in the amide is explained by their further removal from the reaction center. This suggests that in para- and meta-substituted benzamides, the inductive effect of substituents predominates over the effect of conjugation. To this same cause must be ascribed the anomalous position of the OCH_3 group and, to some extent, chlorine, which, as is well known, act inductively as acceptors and as donors in conjugation (-J, M, in the terminology of Ingold). In contrast to the case of acid hydrolysis, the predominating inductive effect of the OCH_3 group during exchange can be explained on the basis that during the attack on the carbonyl carbon, the more basic nitrogen atom more strongly decreases conjugation than does the oxygen atom.

The predominating inductive effect of substituents during exchange with benzamides is confirmed by the fact that the Hammett equation $\log k/k_0 = \rho\sigma$ is followed considerably better if the component, σ_i, which relates only to the inductive effect [11], is introduced into the equation in place of the total substituent constant σ [10] (Fig. 1). In applying this equation, lack of other data made it necessary to use values of σ found for reactions at significantly lower temperatures than those at which the exchange rates were measured.

The inhibition of exchange by ortho substituents is in accordance with the well known polarity-independent inhibition of hydrolysis by an acyl oxygen mechanism with an increase in the strength of benzoic acids and a decrease in the basicity of anilines; it has been explained by steric effects [4].

The presence of catalytic amounts of potassium amide (0.1 N) has no effect on the rate of exchange in benzamide. This must be explained on the basis that, owing to the decreased basicity of the amino group in the amide, the equilibrium $NH_2^- + RCONH_2 = NH_3 + RCO \cdot NH^-$ is strongly shifted to the right, and the anion of the amide, owing to the decreased electrophilic nature of its carbonyl carbon, does not participate in the exchange to any practical extent.

These regularities are in complete agreement with those pointed out by Ingold for the bimolecular hydrolysis of esters by $A_{AC}2$ and $B_{AC}2$ mechanisms [4]. With respect to exchange in amides, they follow the equations:

$$N^{15}H_3 + \underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{C}} - NH_2 \rightleftarrows \overset{+}{N}{}^{15}H_3 - \underset{\underset{R}{|}}{\overset{\overset{O-}{|}}{C}} - NH_2 \rightleftarrows N^{15}H_2 - \underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{C}} + NH_3. \qquad (1)$$

and in the presence of NH_4^+

$$N^{15}H_3 + \underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{C}} - \overset{+}{N}H_3 \rightleftarrows \overset{+}{N}{}^{15}H_3 - \underset{\underset{R}{|}}{\overset{\overset{O-}{|}}{C}} - \overset{+}{N}H_3 \rightleftarrows N^{15}H_3 - \underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{C}} + NH_3 \qquad (2)$$

(2)

*In the presence of a sulfonic acid, the introduction of a nitro group into the para position inhibits hydrolysis of benzamide [7].

with the formation of an intermediate complex or with a single-stage synchronous substitution of one amino group for the other [12].

Mechanisms (1) and (2) are not the only ones possible. From energy considerations, some authors [8, 13] have proposed that in the acid group linked to the amide group, a proton is added to the carbonyl to give $R\overset{+}{C}OHNH_2$, and not to the nitrogen to give $RCO \cdot \overset{+}{N}H_3$, or that both forms form an equilibrium system. Meloche and Laidler [7] have proposed the simultaneous participation of two attacking molecules H_2O and OH^- in alkaline hydrolysis or H_2O and H_3O^+ in acid hydrolysis. Syrkin and Moiseev [14] consider it probable that such interaction of three particles is accomplished in a six-membered intermediate complex.

All of these variants agree equally with the observed regularities of the exchange, and are details of our previously proposed [2] mechanism for nucleophilic substitution with proton transfer, which explains the peculiarities of the exchange of an amino group between the various amino compounds and ammonia. These variants are not distinguishable among themselves without additional detailed kinetic and other physicochemical investigations.

The effect of the concentration of NH_4Cl on the rate of exchange in benzamide is shown in Fig. 2. The rate constant increased linearly up to an NH_4Cl concentration of 4.5 N, but with a further increase in acidity, it decreased. A similar case in which the rate passes through a maximum in 3-5 N acid has been reported by Edward and Meacock [8] for the hydrolysis of benzamides in aqueous HCl and H_2SO_4 and also by other authors [4]. This was explained on the basis that the amide is in its protonated form at the maximum in the rate, so that a further increase in acid concentration decreases the activity of the solvent, which participates in the reaction, without increasing the concentration of this form.

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ALLYL BROMINATION OF COMPOUNDS OF THE CYCLOHEXENE SERIES

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Compounds of the cyclohexene series, which may be obtained by Diels-Alder synthesis, are diverse and readily available. It seemed to us of interest to begin a systematic study of allyl bromination of these compounds with N-bromosuccinimide. The objectives of this investigation were also dictated by the consideration that by bromination and subsequent dehydrobromination it is possible to convert available addition products of diene condensation to the corresponding cyclohexadienes, which may then be used for synthesis of natural products and related substances. Moreover, a study of reactions in which the labile allylic bromine is replaced would significantly facilitate solution of the problem of the synthesis of compounds of the cyclohexane series containing various functional groups.

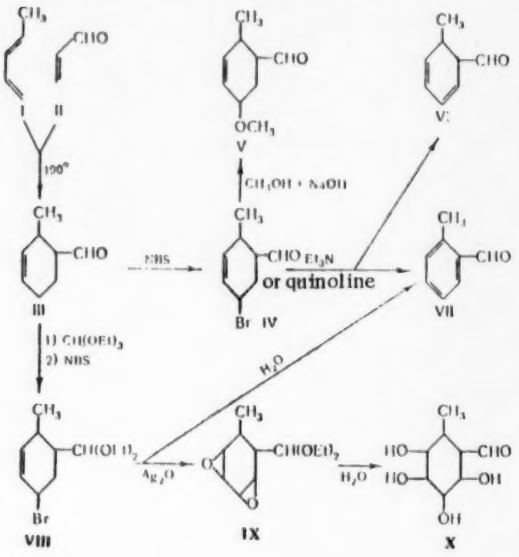
Aldehyde (III) was selected as the first representative of cyclohexene compounds to be investigated; in this connection, it may be remarked that there has been almost no study of the action of N-bromosuccinimide on unsaturated aldehydes [1-3]. The bromination of aldehyde (III) was carried out in solution in boiling carbon tetrachloride in the presence of benzoyl peroxide. The product of the reaction – bromoaldehyde (IV) – was extremely unstable and tended to split out HBr spontaneously.

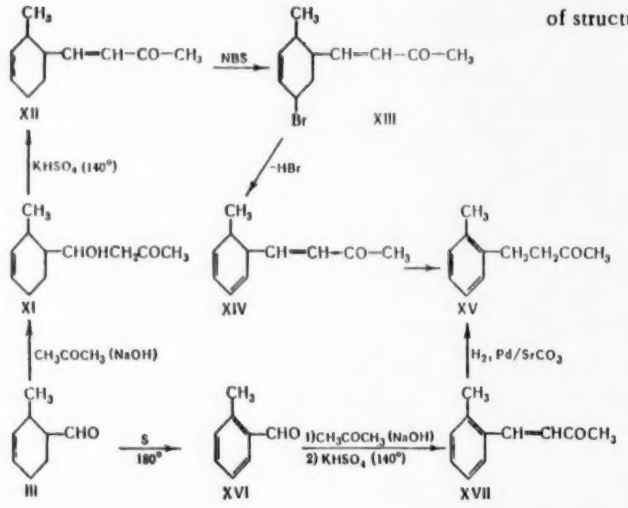
Of the chemical conversions of bromoaldehyde (IV), dehydrobromination under the influence of various agents was given the most study. Dehydrobromination always resulted in the formation of a mixture of substances, which were separated by chromatography and crystallization of the semicarbazones and 2,4-dinitrophenylhydrazones.

Heating bromoaldehyde (IV) with quinoline on a boiling water bath gave only an insignificant amount of the expected cyclohexadiene aldehyde (VI); a large part of the latter underwent further dehydrogenation to o-toluenecarboxaldehyde (VII). Dehydrobromination of the bromo acetal (VIII) with silver oxide (absolute benzene, agitation for 70 hours at 20° in an atmosphere of N_2) and subsequent hydrolysis also gave o-toluenecarboxaldehyde (VII) as the major product. In addition to this compound, methyltetrahydroxycyclohexanecarboxaldehyde (X) was also isolated as the 2,4-dinitrophenylhydrazone; this aldehyde was formed by hydrolysis of the diepoxy acetal (IX). The structure of (X) was confirmed by its I.R. spectrum. However, under milder conditions, dehydrobromination of bromoaldehyde (IV) (refluxing with alcoholic amine) formed predominantly the cyclohexadiene hydrocarbon (VI), while o-toluenecarboxaldehyde (VII) was obtained only in small amounts. Moreover, bromoaldehyde (IV) was converted to methoxycyclohexenecarboxaldehyde (V) by interaction with a methanol solution of potassium hydroxide.

In contrast to the reaction of N-bromosuccinimide with unsaturated aldehydes, the reaction with unsaturated ketones [4, 5], including β-ionone [6-8], has been widely described in the literature. We studied the Δ^3-cyclohexene ketone (XII), which is an analog of β-ionone, and this compound was smoothly brominated by N-bromosuccinimide

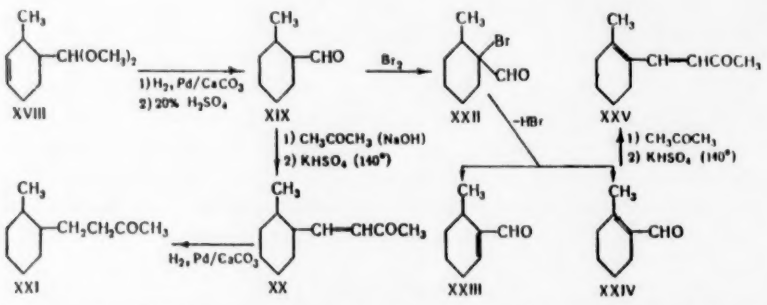
giving exclusively the unstable bromo derivative of the probable structure (XIII), which we were unable to isolate in the pure form. In contrast to bromocyclohexenecarboxaldehyde (IV), bromoketone (XIII) gave only a single product, an alkylaryl ketone (XV), when acted upon by various dehydrobrominating agents (diethylaniline, triethylamine, alcoholic alkali, silver oxide, sodium acetate). It is evident that in this case the initial product of the reaction—cyclohexadiene ketone (XIV)—readily aromatized as a result of a shift of the double bond from the side chain to the ring. It may be remarked that the analogous bromo derivative of β-ionone gives the completely stable cyclohexadiene analog of β-ionone under the influence of dimethylaniline at 80° or silver oxide at room termperature [7, 8]. The stability of the latter compound is associated with the fact that aromatization would require migration of one of the gem-methyl groups; indeed, under more vigorous dehydrobromination conditions (boiling dimethylamine), the alkylaromatic ketone similar in structure to ketone (XV) was obtained [6, 8]. The structure of ketone (XV) was proved by alternate synthesis according to the scheme: (III) → (XVI) → (XVII) → (XV).





The structure of the aldehydes and ketones prepared in the present work were established by a study of the u.v. absorption spectra of their 2,4-dinitrophenylhydrazones; at the same time, we attempted to determine the effect of structure on their light-absorption properties. For the purpose of comparing the light-absorption characteristics of these carbonyl-containing compounds with those of others, we synthesized a series of hydroaromatic aldehydes (XIX, XXIII, XXIV) and ketones (XX, XXI, XXV) having different degrees of unsaturation and different distributions of the double bonds in the molecule.

The resulting absorption curves and the regularities in the relative locations of the absorption maxima found to hold for these 2,4-dinitrophenylhydrazones are in agreement with generalizations reported in the literature relative to the dependence of light-absorption of 2,4-dinitrophenylhydrazones on the structure of the original carbonyl compound [9].



In conclusion, the action of N-bromosuccinimide on 2-methyl-Δ^3-cyclohexenecarboxylic acid (XXVIIa), its methyl ester (XXVIIb), and nitrile (XXVIIc) was studied. It was found that bromination of compounds (XXVIIa-

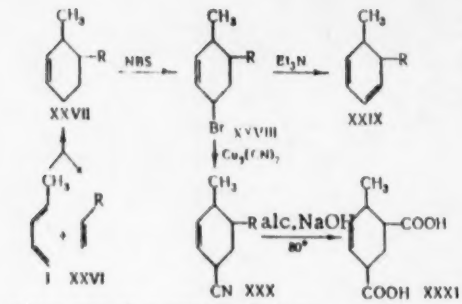
TABLE 1

Compound	B.p., °C/mm	M.p. °C	Refractive Index	Found, % C	Found, % H	Found, % Br	Calculated, % C	Calculated, % H	Calculated, % Br	λ_{max}
IV	125/9.2 (bath)		n_D^{19} 1.5345	48.10	5.69	37.10	47.20	5.42	39.41	
V	77—79/12		n_D^{23} 1.4664	70.21	9.08		70.13	9.09		226
DNPH*		132—135								362
VI DNPH		140—142		54.06	5.08		54.02	4.82		222
										361—363
VII DNPH		193—194		56.08	4.40		56.00	4.00		220—221
										378—384
VIII	100—120/0.4 (bath)		n_D^{25} 1.5075			23.94			28.88	
X DNPH		121.5—123		45.77	4.35		45.40	4.86		
XI	124—125/4	84—86	n_D^{17} 1.4934	72.43	10.07		72.53	9.89		
XII	98—99/3.5		n_D^{18} 1.4985	80.36	9.75		80.48	9.75		
DNPH		144—146		59.32	5.90		59.30	5.81		252
										375—377
XV	85—86/1		n_D^{16} 1.5138	81.50	8.77		81.48	8.64		
DNPH		137.5—138.5		59.45	5.40		59.65	5.26		362
XVII	106.5/0.5		$n_D^{17.5}$ 1.5880	82.59	7.71		82.50	7.50		
DNPH		223—224		60.16	4.77		60.00	4.71		230
										300
										386—388
XVIII	87/14		n_D^{15} 1.4588	70.89	10.68		70.59	10.59		
XIX	58/13		n_D^{19} 1.4480	76.17	10.92		76.18	11.11		
DNPH		152—153.5								229
										360—361
XX	95/4		$n_D^{14.5}$ 1.4841	79.34	10.94		79.52	10.84		
DNPH		143.5—145		58.80	6.37		58.96	6.35		251
										377
XXI	108/12		n_D^{18} 1.4610	78.35	12.01		78.57	11.90		
DNPH		109—111.5		58.74	7.05		58.62	6.89		228
										361
XXXIII										
DNPH		174—176								254
										378—379
XXIV										
DNPH		189—190								257
										384—385
XXV										
DNPH		193—194								230—232
										306
										389
XXVII b	80—82/0.12		n_D^{21} 1.5134	45.90	5.90	34.33	46.35	5.58	34.33	
XXVIIIc	101—102/0.5		n_D^{20} 1.5322	47.94	5.28	39.60	48.00	5.00	40.00	
XXIX	90.5—91.5/14		n_D^{25} 1.4960	71.21	8.05		71.05	7.89		
XXXI		274—275		58.62	6.98		58.69	6.52		

* DNPH = 2,4-dinitrophenylhydrazone.

XXVIIc) proceeds smoothly in a medium of boiling carbon tetrachloride and leads to the formation of the corresponding bromo derivatives (XXVIIIa-XXVIIIc) in good yields. It may also be remarked that using the methyl ester of the acid (XXVIIIb), we showed that bromination by N-bromosuccinimide takes place in the 5 position. This was accomplished by replacing the allylic bromine with a cyano group by means of cuprous cyanide; hydrolysis of the resulting compound (XXX) led to trans-6-methyl-Δ-tetrahydroisophthalic acid (XXXI), which has been described in the literature [10].

In contrast to the other bromo derivatives considered above, dehydrobromination of which did not result chiefly in the formation of a cyclohexadiene system, bromo ester (XXVIIIb) dehydrobrominated to the corresponding cyclohexadiene derivative with rather good yield. Thus bromination and dehydrobromination of ester (XXVIIb)



where XXVI a) R=$COOCH_3$; b) R=CN
XXVII a) R=COOH; b) R=$COOCH_3$; c) R=CN
XXVIII a) R=COOH; b) R=$COOCH_3$; c) R=CN
XXIX R=$COOCH_3$
XXX R=$COOCH_3$

readily led from a compound of the Δ^3-cyclohexene series, obtained by diene condensation, to a compound of the cyclohexadiene series. On this basis, we may say that it is possible that the way has been cleared for synthesis of cycloaliphatic polyenes having structures close to those of natural compounds.

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STEREOISOMERIC 1,4-DI-n-PROPYL- AND 1-METHYL-4 -(2-METHYLBUTYL) CYCLOHEXANES

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We have previously shown [1, 2, 3] that the physical properties of certain 1,4-dialkylcyclohexanes are different from those usually observed in this series. Thus the lower-boiling isomers of 1,4-diisopropyl- and 1,4-di-tert-butylcyclohexane have the cis configuration, while in all other known cases the trans-1,4-dialkylcyclohexanes boil lower. A comparison of these facts with the reliable data available in the literature suggested that the difference in boiling points of stereoisomers ($\Delta t = t_{cis} - t_{trans}$) should vary linearly with molecular weight. The point of intersection with the abscissa of the straight line representing this dependence could explain the inversion in boiling points of stereoisomers at a specific molecular weight [4]. This dependence was obeyed well in the 1,2-dialkylcyclopentane series, as was recently confirmed by new examples [5]. In the 1,2-dialkylcyclohexane series, only the first member of the series deviates from this linear relationship, and this is, perhaps, associated with the more complex geometry of the cyclohexane ring as compared to that of the cyclopentane ring and with the resulting stronger interaction of the 1,2-e,a-groups. Data on the 1,4-dialkylcyclohexanes would also appear to confirm the existence of a linear relationship. However, in contrast to the cases considered above, in this case the scarcity of the available experimental material has made it necessary to use not only hydrocarbons with primary alkyl side chains, but also compounds with secondary radicals–methylisopropyl- and diisopropylcyclohexanes. In other words, the possible effect of the structure of the side chain was not taken into account in this case. The present investigation was undertaken in order to resolve the question of what, precisely, is this effect?

With this aim, the cis and trans isomers of 1,4-di-n-propyl- and 1-methyl-4-(2-methylbutyl) cyclohexanes were synthesized and isolated; these compounds are structural isomers of 1,4-diisopropylcyclohexane, for which boiling point inversion of the stereoisomers was observed. Moreover, these hydrocarbons were selected because in one case the side chains are the same and in the other case they are different. This should show to what extent asymmetry of the radicals can affect the value of Δt. It was found that for the stereoisomers prepared in the present work, the trans form boils below the cis form; i.e., in both cases Δt was positive, while it was negative for the 1,4-diisopropylcyclohexanes [1,4]. Thus, whether a side chain is primary, secondary, or tertiary has a substantial effect on the relationship of the boiling points of stereoisomeric dialkylcyclohexanes. The question of whether a linear relationship exists among the 1,4-dialkylcyclohexanes with primary side chains must remain open until additional experimental data appear.

As in our previous work, synthesis of the hydrocarbons was carried out by methods which made possible preparation of the purest reaction products, even though this was detrimental to the yield. Thus, the 1,4-di-n-propylcyclohexanes were prepared from p-dibromobenzene and allyl chloride by Grignard synthesis and subsequent hydrogenation of the p-diallylbenzene.

Since under ordinary conditions p-dibromobenzene reacts with only one atom of magnesium [6], replace-

ment of the bromine atoms by allyl radicals was carried out in two steps. The 1-methyl-4-(2-methylbutyl) cyclohexanes were prepared from α-chloro-p-xylene by the usual Grignard method.

The addition of hydrogen to the double bond of the intermediate methylbutenyltoluene was carried out at room temperature in the presence of platinum and was accompanied by partial hydrogenation of the benzene ring. However, the p-(2-methylbutyl) toluene, which has not been described in the literature, could be isolated in the pure form by distillation in a column. p-(2-Hydroxy-2-methylbutyl) toluene was also prepared for the first time.

The starting materials were purified very carefully in order to assure a high degree of purity of the final products. Final separation of the stereoisomers was accomplished by vacuum distillation in columns having an efficiency of 100 theoretical plates at very high reflux ratios. The distillation was carried out continuously over a period of a number of days. The distillate was collected in small fractions (3-5 ml each), and the physical constants of each of these were determined. When several successive distillate fractions had the same constants, these fractions were considered to consist of an individual hydrocarbon. The configurations of all four stereoisomers, which have not previously been described in the literature, were determined by means of Raman spectroscopy* on the basis that the spectra of the cis isomers of this series always have an intense line at about 630 cm^{-1} [7]. The physical constants of the stereoisomers and the lines characterizing their configuration are shown in Table 1. For comparison, the table also presents previously published [1] properties of the stereoisomeric 1,4-diisopropylcyclohexanes. The data of Table 1 show that the indices of refraction and the densities of the cis forms were higher in all cases, in agreement with the well-known rule of Auwers-Skita, while the boiling points were higher or lower depending on the structure of the side chains.

TABLE 1

Physical Constants of Stereoisomeric 1,4-Dialkylcyclohexanes of the Composition $C_{12}H_{24}$

Hydrocarbon	Configuration	B.p. °C/mm	B.p. °C/760 mm*	Δt/760 mm	n_D^{20}	d_4^{20}	**MR D	Characteristic spectral lines of the cis form
1,4-Di-n-propylcyclohexane	cis	96,9/14,0	221,0		1,4480	0,8138	55,28	634(13)
	trans	96,1/14,0	220,0	+1,0	1,4440	0,8030	55,59	—
1-Methyl-4-(2-methylbutyl)cyclohexane	cis	97,5/20,0	211,5		1,4469	0,8121	55,36	636(14)
	trans	90,5/16,0	209,0	+2,5	1,4418	0,7997	55,66	—
1,4-Diisopropylcyclohexane	cis	78,9/ 7,5	215,1		1,4524	0,8236	55,17	629(46)
	trans	80,4/ 7,5	217,1	−2,0	1,4485	0,8143	55,38	—

* Calculated using the data of the Dreisbach tables [8].

** MR_D calculated for $C_{12}H_{24}$, 55.42.

Experimental

The p-dibromobenzene was prepared by bromination of benzene with bromine in the presence of $AlBr_3$ and was recrystallized three times from ether; it melted at 87.5°.

The p-bromoallylbenzene was prepared by Grignard synthesis from p-dibromobenzene and allyl chloride in six separate reactions; the yield was 30-51%. After being distilled five times from a Favorskii flask, the p-allylbromobenzene (550.2 g) had the following constants: b. p. 73.0-74.0°/4.5 mm; n_D^{20} 1.5560; d_4^{20} 1.3220.

p-Diallylbenzene. From 508.6 g of freshly distilled p-bromoallylbenzene and 248.6 g of allyl chloride was obtained, by Grignard synthesis, 143.6 g of p-diallylbenzene (yield, 35.2% of theoretical calculated on the p-bromoallylbenzene) having the following constants after four distillations from a Favorskii flask: b. p. 68.0°/3.5 mm; n_D^{20} 1.5420; d_4^{20} 0.9131.

p-Di-n-propylcyclohexanes. p-Diallylbenzene was hydrogenated in a bomb in the presence of platinized carbon activated by the addition of H_2PtCl_6 [9], and then, in order to ensure complete hydrogenation, the cataly-

* All spectroscopic investigations were carried out by our colleagues in the Commission for Spectroscopy OFMN [Division of Physical and Mathematical Sciences] AN SSSR V. T. Aleksanyan and Kh. E. Sterin, to whom we acknowledge our appreciation for this assistance.

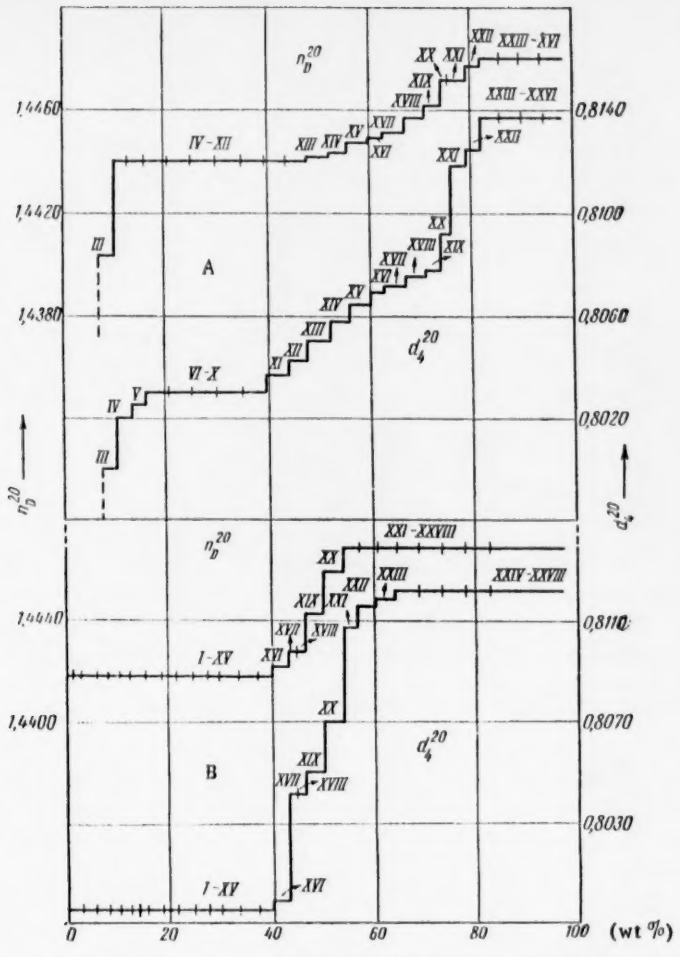

Fig. 1. Refractive indices and densities of fractions of the hydrocarbons investigated. A) 1,4-Di-n-propylcyclohexanes. B) 1-Methyl-4-(2-methylbutyl)cyclohexane.

zate was passed over platinized carbon at 150° in a stream of H_2. The product was chromatographed on silica gel to remove traces of aromatics.

Separation of the stereoisomeric 1,4-di-n-propylcyclohexanes. A mixture of 89.9 g of the chromatographed stereoisomers (n^{20}_D 1.4442; d^{20}_4 0.8070) was distilled in a column at 9-10 mm at a reflux ratio of 200-220. A total of 26 fractions was collected (Fig. 1A); the loss did not exceed 1.8%. The properties of these stereoisomers are presented in Table 1.

α-Chloro-p-xylene was prepared from p-xylene of about 99.9% purity (by freezing point curve) by vapor-phase chlorination under radiation from a 500-watt lamp. The yield in different experiments was 30-50% calculated on the p-xylene. Distillation of the combined reaction products five times from a Favorskii flask gave 334.2 g of α-chloro-p-xylene; b. p., 92.0-92.5°/20 mm; n^{20}_D 1.5340; d^{20}_4 1.0510.

p-(2-Hydroxy-2-methylbutyl) toluene was prepared under the usual Grignard conditions (in an atmosphere of nitrogen) from 61.4 g of magnesium (2.53 g-atoms), 332.0 g of α-chloro-p-xylene (2.38 moles) in 700 ml of absolute ether, and 200 g of freshly distilled methyl ethyl ketone (2.77 moles) in 450 ml of ether. The products were separated in the usual manner and distilled four times from a Favorskii flask, and the resulting p-(2-hydroxy-2-methylbutyl) toluene (220.2 g; yield, 52.1% of theoretical calculated on the α-chloro-p-xylene) had the following properties; b. p., 112.8-113.5°/6.5 mm; n^{20}_D 1.5120; d^{20}_4 0.9562. The composition calculated from the analyt-

ical results was $C_{12}H_{18}O$.

	Found %:	C 80.63;	80.62;	H 10.15;	10.13
$C_{12}H_{18}O$.	Calculated %:	C 80.83;		H 10.18	

p-(2-Methyl-1-butenyl)toluene. A mixture of 200.0 g of p-(2-hydroxy-2-methylbutyl)toluene (1.12 moles) and 69.2 g of boric acid (1.12 moles) was heated in a flask fitted with a reflux condenser for 3 hours [10] and was then decanted. The product was dried with calcium chloride and distilled from a Favorskii flask; 147.5 g of a mixture of p-methylbutenyltoluenes was obtained (yield, 81.0%). The material had the following constants: b. p. 102.0-104.0°/13 mm; $n^{20}D$ 1.5160; d^{20}_4 0.8836. No data for these hydrocarbons appear in the literature.

p-(2-Methylbutyl) toluene. A portion of the methylbutenyltoluene (50.5 g) was hydrogenated in a bomb as described above. Then, 49.3 g of the catalyzate was distilled in a column at 12.5 mm at a reflux ratio of 180-200, and 25.7 g of p-(2-methylbutyl) toluene was collected in 12 fractions which had the same constants: b. p., 92.5°/12.5 mm; $n^{20}D$ 1.4899; d^{20}_4 0.8497.

1-Methyl-4-(2-methylbutyl) cyclohexanes. The p-(2-methylbutyl) toluene (110.5 g) was hydrogenated by passage over platinized carbon at 150° in a stream of H_2, and the catalyzate was chromatographed on silica gel for removal of traces of aromatics.

Separation of the stereoisomeric 1-methyl-4-(2-methylbutyl) cyclohexanes. A mixture of 105.1 g of the chromatographed stereoisomers (b. p., 81.5-82.5°/11 mm; $n^{20}D$ 1.4450; d^{20}_4 0.8159) was distilled in a column at 10-12 mm and a reflux ratio of 200-220° (during collection of fractions with constant refractive indices and densities, the reflux ratio was decreased to 150-180°). A total of 28 fractions was collected (Fig. 1B); the loss did not exceed 2.8%. The properties of these stereoisomers are shown in Table 1.

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**See C. B. translation.

INTERACTION OF CYCLOPENTADIENYLSODIUM WITH ALKOXYTITANIUM CHLORIDES

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Mono-π-cyclopentadienyl derivatives of titanium—cyclopentadienyltriethoxytitanium and cyclopentadienyltripropoxytitanium—were obtained during our investigation of the reaction of cyclopentadienylsodium with alkoxytitanium chlorides:

$$2\ Cl_2Ti(OC_2H_5)_2 + 3C_5H_5Na \longrightarrow C_5H_5Ti(OC_2H_5)_3 + (C_5H_5)_2Ti\langle^{OC_2H_5}_{Cl} + 3NaCl,$$

$$ClTi(OC_3H_7)_3 + C_5H_5Na \longrightarrow C_5H_5Ti(OC_3H_7)_3 + NaCl.$$

These substances are colorless liquids, and can be distilled under vacuum (b. p. of $C_5H_5Ti(OC_2H_5)_3$ 106-107°C /3 mm, $n^{20}D$ 1.5500; b. p. of $C_5H_5Ti(n\text{-}C_3H_7O)_3$ 106-107°C /0.5-1 mm, $n^{20}D$ 1.5272). They are very sensitive to the action of atmospheric moisture.

	Found %:	C 52.87;	52.90;	H 8.23;	8.19;	Ti 19.18;	19.00
$C_5H_5Ti(OC_2H_5)_3$.	Calculated %:	C 53.23;		H 8.12;		Ti 19.30.	

Molecular weight: found (cryoscopically in benzene), 236 and 238; calculated, 248.

	Found %:	C 57.60;	57.69;	H 9.17;	9.10;	Ti 16.34;	16.03
$C_5H_5Ti(OC_3H_7)_3$.	Calculated %:	C 57.92;		H 9.02;		Ti 16.50.	

Molecular weight: found, 282; calculated, 290.

It is interesting that, in contrast to the usual alkoxy derivatives of titanium which characteristically are associated in solution [1-6], π-cyclopentadienyltrialkoxytitanium compounds are not associated in solution, and even at a concentration of 1.7 mole % the molecular weight of $C_5H_5Ti(OC_2H_5)_3$, as determined cryoscopically in benzene, corresponds to that calculated for the monomeric compound. The structure of π-cyclopentadienyltriethoxytitanium and π-cyclopentadienyltri-n-propoxytitanium was proved by conversion to cyclopentadienyltitanium trichloride, which has been described in the literature [7, 8]:

$$C_5H_5Ti(OR)_3 + 3CH_3COCl \rightarrow C_5H_5TiCl_3 + 3CH_3COOR,$$

where R = C_2H_5; p-C_3H_7.

Moreover, the infrared spectra of these compounds contained a band at about 770 cm^{-1}, which is characteristic of all three titanium derivatives with a single π-cyclopentadienyl ring which have been described in the literature [8].

When ethoxytitanium trichloride was used in the reaction with cyclopentadienylsodium, the reaction proceeded according to the equation:

$$Cl_3TiOC_2H_5 + 2C_5H_5Na \rightarrow (C_5H_5)_2\,Ti\,(OC_2H_5)\,Cl + 2NaCl.$$

	Found %:	C 56.02; 55.74;	H 5.77; 5.97;	Ti 18.39; 18.69	
		Cl 13.47; 13.85			
$(C_5H_5)_2TiCl(OC_2H_5)$.	Calculated %:	C 55.72;	H 5.84;	Ti 18.52.	
		Cl 13.70.			

Molecular weight: found (cryoscopically in benzene), 250; calculated, 258. M. p. of $(C_5H_5)_2Ti(OC_2H_5)Cl$ 91-92°.

We also found that alcohols decompose π-cyclopentadienylalkoxytitanium compounds under mild conditions (heating for an hour at a bath temperature of 70-80°), forming the corresponding tetraalkoxytitanium and cyclopentadiene:

$$C_5H_5Ti\,(OC_2H_5)_3 + ROH \rightarrow (RO)_4\,Ti + C_5H_6,$$

where R = C_2H_5; p-C_3H_7.

The cyclopentadiene was isolated as cyclopentyldienylthallium.

	Found %:	C 22.29; 22.25;	H 1.85; 1.84	
C_5H_5Tl.	Calculated %:	C 22.29;	H 1.87	

Alkoxy chlorides of π-cyclopentadienyltitanium were obtained by reacting π-cyclopentadienyltri-n-propoxytitanium with acetyl chloride:

$$C_5H_5Ti\,(OC_3H_7)_3 + CH_3COCl \rightarrow C_5H_5Ti\,(OC_3H_7)_2\,Cl + CH_3COOC_3H_7,$$
$$C_5H_5Ti\,(OC_3H_7)_3 + 2CH_3COCl \rightarrow C_5H_5Ti\,(OC_3H_7)\,Cl_2 + 2CH_3COOC_3H_7$$

1. The cyclopentyldienyldi-n-propoxytitanium chloride disproportionated when distilled under vacuum (1 mm).

	Found %:	C 49.77; 49.61;	H 7.84; 7.65;	Ti 17.50; 17.64	
$C_5H_5Ti(OC_3H_7)_2Cl$.	Calculated %:	C 49.55;	H 7.18;	Ti 17.96	

Molecular weight: found, 270; calculated, 267.

2. Cyclopentadienyl-n-propoxytitanium dichloride, b.p. 159-161°/2 mm.

	Found %:	C 39.23; 39.36;	H 4.99; 5.12;	Ti 28.85; 29.57;	28.98;
		Cl 19.52; 19.14			
$C_5H_5Ti(OC_3H_7)Cl_2$.	Calculated %:	C 39.54;	H 4.97;	Ti 29.18;	
		Cl 19.71.			

Molecular weight: found, 238; calculated, 243.

These substances are greenish yellow, viscous liquids which decompose under the action of atmospheric moisture, but which are stable when stored at low temperatures. Their infrared spectra also contain an absorption band at about 770 cm^{-1}.

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SPECTROPOLARIMETRIC INVESTIGATION OF THE KETIMIDE-ENAMINE TAUTOMERIC SYSTEM

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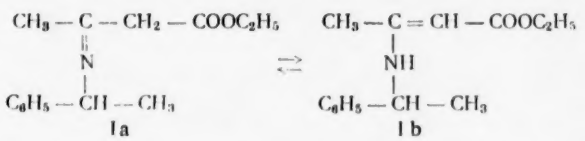
Having observed the peculiar effect of the solvent on the optical rotatory dispersion of N-benzoyl-α-phenethylamine and having explained these observations from the point of view of amide-iminol tautomerism [1], we became interested in the possibility of using the spectropolarimetric method for the study of other cases of tautomerism. The first subject selected for investigation was the product of the condensation of optically active α-phenethylamine with acetoacetic ester, which would be expected to exhibit ketimide-enamine tautomerism according to the scheme:



Ia Ib

The condensation was carried out at a temperature of 10-15° in ether solution in the manner described for benzylamine [2], and two substances were obtained having the same elemental composition, which corresponded to Formula I: a liquid which distilled under vacuum (150-152°/2 mm) and crystals which melted at 64-78°. An accurate determination of the melting point was impossible, since the crystals were stable only below zero; when they were stored at room temperature, within 10-12 hours the crystals had changed to a liquid which had the same rotation as the liquid portion of the condensation product.

Attempts to carry out the reverse transition—to convert the liquid to the solid form—were unsuccessful; however, the presence of an equilibrium (and not just a unidirectional transition) was indicated by the mutarotation of solutions of the solid and liquid form in 65% aqueous methanol; it was found that the two systems tended toward the same equilibrium state from different directions (see Fig. 1).

The fact of the conversion does not, of itself, prove the existence of ketimide-enamine tautomerism, since this conversion could also be connected with syn-anti transition of ketimide form Ia or cis-trans transition of enamine form Ib. However, the establishment of the reversibility of the transition seemed to us weighty evidence in support of the presence of ketimide-enamine tautomerism, since in the case of syn-anti or cis-trans isomerism, spontaneous reaction is observed only in one direction; in the latter two cases, the labile form spontaneously converts to the stable form, and the reverse transformation requires the consumption of energy and ordinarily does not proceed spontaneously.

It was possible to obtain an answer to the question of just what the solid form* is by comparing its optical

*We consider the solid rather than the liquid form, because the latter obviously must be a mixture, and not an individual substance.

with the rotation of substances having known structures. Solutions of the solid form in all solvents showed a rapid change in rotation with time (Fig. 2); however, the initially observed (or extrapolated to initial time, $\tau = 0$) rotation in all cases had a negative sign, i.e., the same sign as had the rotation of the original amine. Schiff bases prepared by condensation of aliphatic aldehydes (acetic, isobutyric) with optically active (−) α-phenethylamine

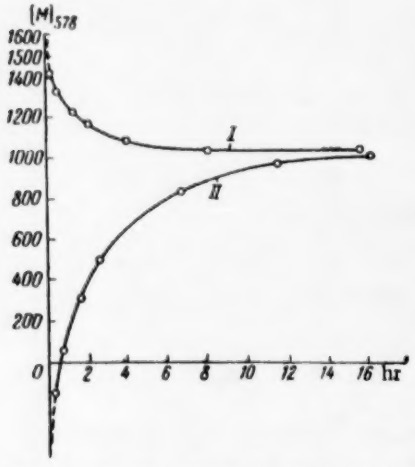


Fig. 1. Mutarotation of the liquid (I) and of the solid (II) in 65% methanol.

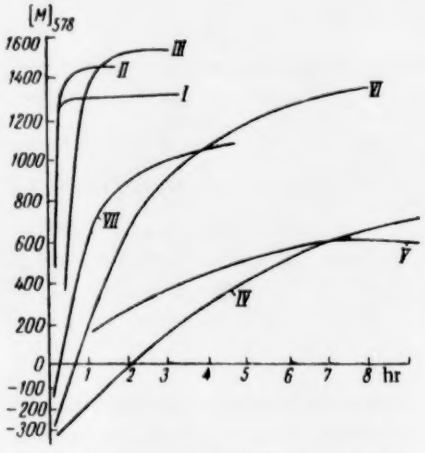
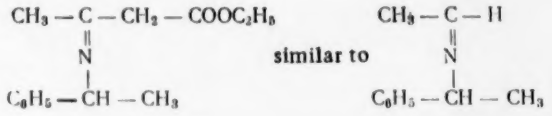


Fig. 2. Mutarotation of the crystalline form: I) in dioxane, II) in carbon tetrachloride, III) in benzene, IV) in methanol, V) in alcohol, VI) in ethyl acetate, VII) in a 65% solution of ethylene glycol in methanol.

exhibit the same change in rotation. This provides a basis for the conclusion that the solid form resembles a Schiff base in structure, i.e., it is a ketimide:



It is also apparent from Fig. 2 that the rate at which equilibrium was reached depended to a great extent on the solvent; equilibrium was established slowly in polar solvents (23 hours in methanol) and rapidly in nonpolar solvents (50 minutes in dioxane).

There are a number of reports in the literature relating to the effect of the solvent on tautomeric systems; however, these treat chiefly keto-enol tautomerism. Thus the work of A. N. Nesmeyanov and M. I. Kabachnik [3] indicated that the position of a tautomeric equilibrium depends on the relative basicity (or acidity) of the form in the given medium. In particular, in the system β-aminocrotonic−iminoacetic ester, the equilibrium is shifted toward the less basic form, which, in this case, is the amine form. In order to determine the effect of solvents having a basic or acidic nature on the equilibrium in the present tautomeric system, we obtained curves of the rotatory dispersion of the liquid form in pyridine and in acetic acid (in the equilibrium state) and compared them with the rotatory dispersion curves of ethyl β-(α-phenethylamino)butyrate, which was synthesized for this purpose. Comparing the dispersion curves, which are shown in Fig. 3, it may be seen that the product of the condensation of α-phenethylamine with acetoacetic ester, which is capable of ketimide-enamine tautomerism, exhibited a sharp change in rotation, both in magnitude and sign, during the transition from a basic to an acid solvent. At the same time, the small difference between the rotation of the ethyl β-(α-phenethylamino)butyrate in pyridine and that in acetic acid shows that the change in rotation in the first case is not simply a consequence of salt formation; the obvious reason is that the acid solvent shifts the equilibrium in the direction of the (more basic) ketimide form Ia, combining it in the form of a salt. The basic solvent led to a predominance of enamine form Ib.

Additional confirmation of these conclusions was obtained through the use of the method of azo compounds,

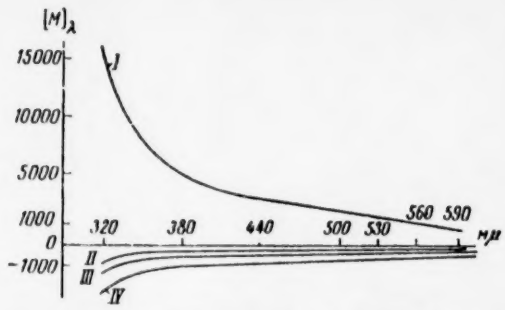


Fig. 3. Rotatory dispersion of: the liquid phase in pyridine (I) and in acetic acid (II); ethyl β-(α-phenethylamino)butyrate in acetic acid (III) and in pyridine (IV).

which was once used by Dimroth [4] to investigate keto-enol systems, and the bromination method, which was recently used by Seher [5] to study the tautomerism of β-aminocrotonic ester, although the applicability of the latter method to enamines has been doubted [6]. Both methods showed that the amount of enamine in solutions of the solid form was initially small and gradually increased; i.e., the result of the polarimetric investigation was qualitatively confirmed.

Using the value of the rotation of the equilibrium system, it is possible to calculate the composition of the equilibrium mixture if the values of the rotation of the individual components of the system are known. The rotation of one of the components—the solid ketimide form—was easily found by extrapolation to $\tau = 0$ of the mutarotation curve for a given solvent. Such extrapolation for the solution in 65% methanol gave a value of $[M]_{578}^{\text{ketimide}}$ of −350° (see Fig. 1). Similarly, extrapolation of the mutarotation curve for the liquid form in the same solvent gave a rotation for this form of $[M]_{578}^{\text{liq}}$ of +1600°. However, in contrast to the solid form, in the present case there is no assurance that the liquid form is an individual (enamine) form and not a mixture of the ketimide and enamine forms or a mixture of geometric isomers of the latter. If it is assumed that the liquid form is entirely one specific geometric isomer of the enamine form (most probably, the cis form stabilized by hydrogen bonding), then calculations based on the rotation values presented above indicate an enamine content of 68% in the equilibrium mixture in 65% methanol. This almost coincides with the percent enamine (69%) found by Seher [5] for a methanol solution of β-aminocrotonic ester.

These results indicate good prospects for the use of the spectropolarimetric method in studies of tautomeric systems. In continuing our investigations along this line, we shall in particular extend the application of this method to keto-enol systems of the type of acetoacetic ester, in addition to applying it to a study of the behavior of amides and ketimide-enamine systems.

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SOME REACTIONS OF BISCYCLOPENTADIENYLDIPHENYLTITANIUM

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Biscyclopentadienyl derivatives of titanium of the type $(C_5H_5)_2TiX_2$, where X is halogen, form complexes with aluminum alkyl and aryl compounds which are used as Ziegler-type catalysts for the polymerization of α-olefins. The halogen atom in these compounds is labile, as indicated by halogen exchange reactions [1] and by replacement of the halogen by a hydrocarbon radical which links to the titanium by a σ-bond. The alkyl compounds are unstable, and are prepared with considerable difficulty [2]. The aryl derivatives are more stable, but there has been almost no study of their chemical properties.

It seemed to us to be of interest to compare certain chemical properties of $(C_5H_5)_2 Ti Ar_2$, in which the $(C_5H_5)_2Ti$ group may be likened to a metal, with the properties of other organometallic compounds. Radical-halogen exchange reactions are widely used to compare the reactivities of organometallic compounds. We decided to carry out this type of reaction for $(C_5H_5)_2TiCl_2$ and $(C_6H_5)_2Hg$, on the one hand, and for $(C_5H_5)_2(C_6H_5)_2$ and $HgCl_2$, on the other.

The first system was studied by heating the components in boiling benzene or methylene chloride for 6 hours. At the end of this time, about 20% of the expected phenylmercury chloride was separated from benzene solution; in methylene chloride solution, the yield of phenylmercury chloride was almost theoretical in spite of the fact that the reaction temperature was significantly lower:

$$(C_5H_5)_2 TiCl_2 + 2(C_6H_5)_2 Hg \rightarrow (C_5H_5)_2 Ti(C_6H_5)_2 + 2C_6H_5HgCl. \quad (1)$$

Under the conditions used, the second product – $(C_5H_5)_2Ti(C_6H_5)_2$ – reacted further, and, therefore, could not be isolated.

The interaction of biscyclopentadienyldiphenyltitanium and mercuric chloride was carried out by stirring the components in benzene or CCl_4 solution at 80° in an atmosphere of nitrogen. The reactant ratio $(C_5H_5)_2Ti(C_6H_5)_2$ / $HgCl_2$ was varied from 1 : 1 to 1 : 2, and the yield of products was higher in the latter case. The major reaction products were biscyclopentadienyltitanium dichloride and phenylmercury chloride; the ratio of these products was 1 : 2 in all experiments. In the best case, in which the reaction was carried out in carbon tetrachloride, 0.0145 mole of $(C_5H_5)TiCl_2$ and 0.0281 mole of C_6H_5HgCl were obtained from 0.021 mole of $(C_5H_5)_2 Ti(C_6H_5)_2$ and 0.042 mole of $HgCl_2$. Hence, it may be concluded that the chief reaction (which occurs to the extent of about 70%) is an exchange between biscyclopentadienyldiphenyltitanium and mercuric chloride in accordance with the equation:

$$(C_5H_5)_2 Ti(C_6H_5)_2 + 2HgCl_2 \rightarrow (C_5H_5)_2 TiCl_2 + 2C_6H_5HgCl. \quad (2)$$

The amount of these products formed in benzene solution was considerably different; the yield of biscyclopentadienyltitanium dichloride dropped to 24%, and the amount of phenylmercury chloride increased to 90%. The quantitative determination of the organotitanium compound was carried out spectrophotometrically.

When the reaction was carried out in CCl_4 solution, chlorobenzene, biphenyl, and mercurous chloride were obtained in addition to the major products. Phenol was formed when the reaction was carried out in the presence of atmospheric oxygen. Chlorobenzene was not found when the reaction was carried out in benzene, and the yield of biphenyl was increased. The formation of these products can be explained by a parallel interaction of the original organotitanium compound with the solvent. Processes of this type would explain the absence of $(C_5H_5)_2Ti(C_6H_5)_2$ from the products of Reaction (1) and also the sharp increase in the yield of phenylmercury chloride in methylene chloride medium.

This compelled us to carry out the decomposition of $(C_5H_5)_2Ti(C_6H_5)_2$ in various solvents. The reaction of biscyclopentadienyldiphenyltitanium in benzene was especially interesting. In carrying out this reaction, care was taken to exclude atmospheric oxygen; the tubes containing the original solution were sealed under vacuum. When these tubes were heated, there was a sharp change in color from the original yellow to a dark green, which is characteristic of compounds in which the titanium is in a lower valence state. It is known that the paramagnetic form of biscyclopentadienyltitanium, which has been briefly described in the literature [4], possesses a dark green color. In our case, paramagnetism was shown by e.p.r. spectroscopy. Biscyclopentadienyltitanium dichloride, chlorobenzene, and a small amount of biphenyl were obtained from the reaction in CCl_4. The formation of chlorobenzene and biphenyl is common for reactions of phenyl radicals in carbon tetrachloride [5]. It may be assumed that the $Ti-C_6H_5$ bond initially splits homolytically to yield free phenyl radicals.

With the aim of confirming this assumption, $(C_5H_5)_2Ti(C_6H_5)_2$ was reacted with alcohols (methyl and isopropyl) and with chloroform. In the first case, benzene and products resulting from dehydrogenation of the alcohol by phenyl radicals (formaldehyde or acetone) were formed quantitatively. The solution acquired an intense green color due to the formation of $(C_5H_5)_2Ti$. Thermal and photochemical reactions in chloroform gave benzene, an almost quantitative yield of $(C_5H_5)_2TiCl_2$, and a small amount of biphenyl.

The above results suggest the following mechanism for reactions of biscyclopentadienyldiphenyltitanium. When heated or irradiated with ultraviolet, the original titanium compound decomposes with the liberation of phenyl radicals and the formation of dark green, paramagnetic biscyclopentadienyltitanium:

$$(C_5H_5)_2\,Ti\,(C_6H_5)_2 \rightarrow (C_5H_5)_2Ti + 2C_6H_5\cdot$$

This stage is reminiscent of the decomposition of diphenylmercury, the role of metallic mercury being played by the extremely reactive compound of divalent titanium.

The behavior of the resulting phenyl radicals depends on the solvent; in benzene, the phenyl radicals yield biphenyl, while in chloroform or alcoholic solutions, hydrogen is removed with the formation of benzene:

$$2C_6H_5\cdot + CH_3OH \rightarrow 2C_6H_6 + CH_2O;$$
$$2C_6H_5\cdot + CH_3CHOHCH_3 \rightarrow 2C_6H_6 + CH_3COCH_3;$$
$$C_6H_5\cdot + CHCl_3 \rightarrow C_6H_6 + \cdot CCl_3.$$

The phenyl radical forms chlorobenzene in CCl_4:

$$C_6H_5\cdot + CCl_4 \rightarrow C_6H_5Cl + \cdot CCl_3.$$

Biscyclopentadienyltitanium remains unchanged in benzene or in alcohols in the absence of atmospheric oxygen.

It is rapidly oxidized to the dichloride in the presence of CCl_4 or chloroform:

$$(C_5H_5)_2Ti + 2CCl_4 \rightarrow (C_5H_5)_2\,TiCl_2 + 2\cdot CCl_3.$$

This reaction was carried out by adding CCl_4 to a green benzene solution of $(C_5H_5)_2Ti$. The green color changed rapidly to red, which is characteristic of the dichloride. The latter was separated from solution and characterized.

A similar reaction occurs in the presence of mercuric chloride.

$$(C_5H_5)_2\,Ti + 2HgCl_2 \rightarrow (C_5H_5)_2\,TiCl_2 + Hg_2Cl_2.$$

This process must be the explanation for the formation of mercurous chloride during the exchange reaction between $(C_5H_5)_2Ti(C_6H_5)_2$ and mercuric chloride. The conversion of $(C_5H_5)_2Ti$ to the dichloride by the action of HCl in the absence of air has been described in the literature [4].

All of these reactions are very reminiscent of thermal and photochemical reactions of diphenylmercury with alcohols, carbon tetrachloride, and chloroform, which take place by a free radical mechanism.

The presence of phenyl radicals during the decomposition of biscyclopentadienyldiphenyltitanium was confirmed by reaction with metallic mercury in a medium of carbon tetrachloride. The formation of phenylmercury chloride is reliable proof of the formation of phenyl radicals at the surface of the metallic mercury:

$$(C_5H_5)_2\,Ti\,(C_6H_5)_2 + Hg + CCl_4 \rightarrow C_6H_5HgCl + (C_5H_5)_2\,TiCl_2 + C_6H_5Cl.$$

Moreover, the presence of free phenyl radicals was confirmed when solutions of α,α-diphenyl-β-picrylhydrazine in benzene, alcohol, and carbon tetrachloride were decolorized by $(C_5H_5)_2Ti(C_6H_5)_2$. Careful removal of atmospheric oxygen during the experiments was extremely important. The dark green color of solutions of dicyclopentadienyltitanium momentarily disappeared in the presence of even traces of oxygen, and light-colored, noncrystalline precipitates containing titanium and cyclopentadienyl groups were formed; these precipitates were apparently oxidation products of the latter.

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INVESTIGATION OF THE SOLUBILITY OF BORIC ACID IN SATURATED STEAM

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In using solutions of boric acid for controlling reactivity of boiling solutions, it is necessary to know the solubility of boric acid in steam as well as in water.

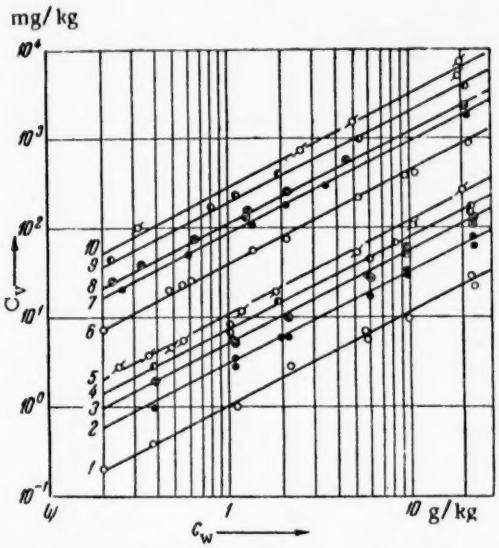

Fig. 1. Variation in the solubility of boric acid in saturated steam with its content in water at the following pressures (in atm): 1) p = 1, 2) p = 3, 3) p = 5, 4) p = 7, 5) p = 10, 6) p = 40, 7) p = 80, 8) p = 100, 9) p = 150, 10) p = 200

Investigations of the solubility of boric acid in saturated steam were carried out in a special apparatus by evaporating a very small amount of solution of a given concentration. Measures were taken in the design of the apparatus to ensure minimum entrainment of drops of water by the steam, and there was a steam jacket to prevent condensation of the vapor on the walls. The boric acid content of the condensate samples was determined colorimetrically using carmine and volumetrically by means of mannitol. The investigation was carried out in a manner designed to provide acceptable accuracy. The relative error was 2-5% in most of the experiments.

The investigation (see Fig. 1) covered a very broad range of pressures (from 1 to 200 atm); this pressure range is of interest not only for boiling-water reactors, but also for vaporizers in atomic energy power plants and also for geothermal stations. The concentration of boric acid in the water was also varied over a wide range (from 0.2 to 22 g/kg).

The investigation disclosed that there is a linear relationship between B_2O_3 concentration in saturated steam and its concentration in water. Consequently, the distribution coefficient for boric acid between the vapor and liquid phases of the solvent does not depend on concentration over the range investigated. Compared to other inorganic compounds, boric acid is very soluble in saturated steam, even at low pressures.

The experimental values of the apparent distribution coefficients of boric acid are shown in Fig. 2 as a function of the ratio of the densities of the solvent phases [2]. This relationship may be expressed for boric acid as an exponential function:

$$K_d^{app} = \frac{C_v}{C_w} = \left(\frac{\gamma_v}{\gamma_w}\right)^{0.885},$$

where C_v and C_w are the concentrations of B_2O_3 in the vapor and water, and γ_v and γ_w are the vapor and water densities, respectively. It may be seen from Fig. 2 that the values of the distribution coefficient fall on the same line as the points obtained at the Moscow Institute of Energetics. It is remarkable that the relationship indicated above holds down to 1 atm, although at a temperature of 200-210° (in the pressure region of 16-20 kg/sq cm), the form of the solid phase which precipitates from a saturated solution of boric acid in water changes. Fig. 2 also shows that of all the compounds studied, boric acid is characterized by the lowest value of K_d^{app} and, correspondingly, the lowest exponent, n = 0.885. Even for silicic acid, n = 1.9. This is associated with the fact that boric acid is a very weak acid ($K_{diss} = 7 \cdot 10^{-10}$), and, like silicic acid, it is practically undissociated in aqueous solution. Therefore, the experimental data once again confirm the theoretical position [3] that compounds which exhibit a greater tendency to transfer to the vapor phase are those which exist as molecules in aqueous solution. This is also indicated by the results of experiments (see Fig. 3) carried out with binary solutions in which one of the components was boric acid. The addition of significant amounts of NaCl or Na_2SO_4 to aqueous solutions of boric acid had practically no effect (at constant pressure) on the apparent distribution coefficient of boric acid. Apparently, it can change only at very high concentrations where the effect of depression begins to affect the ratio γ_v/γ_w.

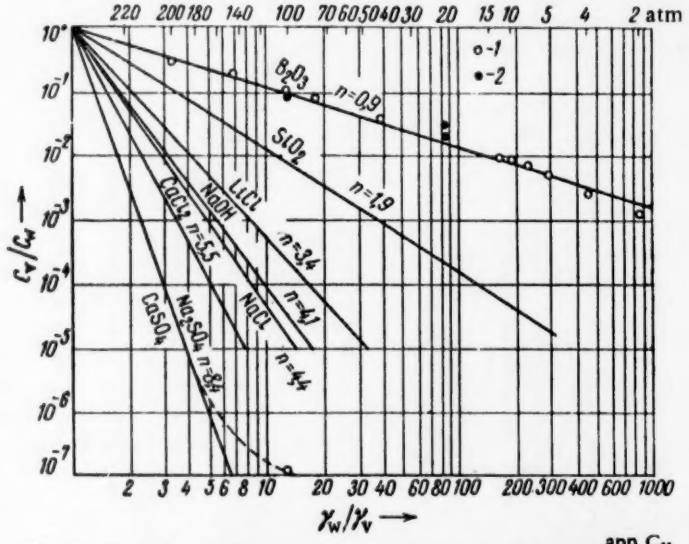

Fig. 2. Variation of the apparent distribution coefficient $K_d^{app} \frac{C_v}{C_w}$ with steam pressure p ratio of vapor to water density γ_v/γ_w. 1) Data of the Institute of Energetics, Academy of Sciences Georgian SSR; 2) data of the Moscow Institute of Energetics.

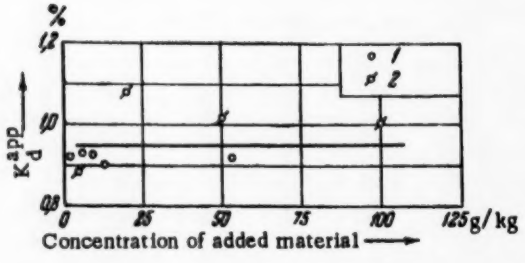

Fig. 3. Dependence of K_d^{app} of boric acid on added material: 1) NaCl, 2) Na_2SO_4. 10 atm pressure.

A number of practical conclusions may be formed as a result of the present work and on the basis of the behavior of boric acid in superheated steam [4]. The behavior of boric acid in the steam line of an atomic energy power plant, including the apparatus for vaporization of purge steam, is completely determined by the laws governing its solubility in steam, since even at atmospheric pressure, the distribution coefficient many times exceeds the usual values of the coefficient of mechanical entrainment of water by steam.

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CONDENSATION OF HEXAMETHYLDISILOXANE IN A SONIC-FREQUENCY, HIGH-VOLTAGE SILENT DISCHARGE

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Organosilicon compounds containing alternating silane-hydrocarbon (−Si−$(CH_2)_n$−Si−) or siloxane (−Si−O−Si−) groups in the main chain can be prepared by several routes. However, some of these routes are merely laboratory methods [1-3], and the proposed hydrolytic [4-7] and catalytic [8, 9] methods start either with relatively unavailable compounds or with compounds which must first be prepared by organometallic synthesis. The use of an electrical discharge for the preparation of compounds with alternating units, provided the problems involved could be solved, would yield a simple, new, single-stage process suitable for commercial production.

It has previously been shown by one of us [10, 11] that it is possible to prepare polymeric compounds containing alternating Si and C atoms in the main chain through the action of a silent discharge of ordinary frequency (50 cps) on methylchlorosilanes.

It has also been shown recently [12] that it is possible to condense hexamethyldisiloxane in electrical discharges to form polymeric compounds of relatively low molecular weight. It seemed of interest, therefore, to attempt to carry out a similar condensation under conditions analogous to those generally used in carrying out catalytic and pyrogenetic processes, i.e., with a single pass of the organosilicon compound through the discharge zone. Owing to the short residence time of the original compounds in the discharge zone, secondary processes should be held to a minimum. In this manner, it should be possible to obtain compounds which result from the primary reactions and thereby to progress toward an explanation of the mechanism of the chemical processes taking place.

A compositionally simple and available compound−hexamethyldisiloxane−was selected as the first object of investigation. On the basis of previously established facts [10-12], it would be expected that the first effect of a silent discharge on hexamethyldisiloxane would be rupture of an Si−CH_3 bond (64 kcal/mole), which is less stable energy-wise than the remaining bonds, Si−O (117 kcal/mole) and C−H (85.5 kcal/mole) [14]. In order to obtain a discharge of sufficient power, the current supplied to the discharge tube in our experiments had a frequency of 4000 cps.

Conditions were selected which would permit collection of condensate with good yields of low-molecular weight condensation products, namely: a voltage of 50 kv and a siloxane feed rate of 8-9 ml/hour. A total of 570 g of hexamethyldisiloxane was charged, and, after distillation of the unreacted hexamethyldisiloxane, 287 g of liquid condensation products was obtained; this corresponds to a yield of 51%. The condensate consisted chiefly (60-70%) of compounds containing 4-6 Si atoms in the molecule. Approximately 10% of the condensate consisted of lower-boiling compounds (with 2-3 Si atoms in the molecule), while high-boiling polymers formed 20-25% of the condensate.

A number of individual compounds were separated by fractionation of the condensate: I) octamethyltrisiloxane, II) 2,2,4,4,6,6,8,8 -octamethyl-2,4,6,8-tetrasila-3,7-dioxanonane, III) 2,2,4,4,7,7,9,9-octamethyl-2,4,7,

9-tetrasila-3,8-dioxadecane, IV) 2,2,4,4,6,6,8,8,10,10, 12, 12-dodecamethyl-2,4,6,8,10,12-hexasila-3,7,11-trioxatridecane, and V) a mixture of high-molecular-weight polymers having the composition $C_{86}H_{242}O_{17}Si_{34}$. The condensate also contained a large number of intermediate fractions consisting of difficulty separable mixtures of various polymers.

The presence in the off-gas of acetylene, which could have been formed only by rupture of Si–CH_3 bonds, and the structures of the individual compounds suggest the following concept of the chemistry of the processes occurring during the course of the reaction. Under the influence of the electrical discharge, the first occurrence is the rupture of Si–CH_3 bonds with the formation of two free radicals:

$$(CH_3)_3Si-O-Si(CH_3)_3 \rightarrow \dot{C}H_3 + \dot{S}i(CH_3)_2-O-Si(CH_3)_3.$$

The resulting methyl radicals are partially or completely converted to acetylene:

$$2\dot{C}H_3 \rightarrow CH \equiv CH + 4\dot{H}.$$

Subsequent reactions probably proceed chiefly with the participation of hydrogen atoms formed as above:

$$(CH_3)_3\,Si-O-\,Si\,(CH_3)_3 + \dot{H} \rightarrow H_2 + (CH_3)_3\,Si-O-(CH_3)_2\,Si\dot{C}H_2$$

or participation of the methyl radicals:

$$(CH_3)_3\,Si-O-Si\,(CH_3)_3 + \dot{C}H_3 \rightarrow CH_4 + (CH_3)_3\,Si-O-(CH_3)_2\,Si\dot{C}H_2.$$

The formation of polymers takes place by recombination of various free radicals, for example:

$$(CH_3)_3\,Si-O-(CH_3)_2\dot{S}i + \dot{C}H_2Si\,(CH_3)_2-O-Si\,(CH_3)_3 \rightarrow$$
$$\rightarrow (CH_3)_3\,Si-O-(CH_3)_2Si-CH_2-Si\,(CH_3)_2-O-Si\,(CH_3)_3 \quad (II)$$

or

$$2(CH_3)_3\,Si-O-(CH_3)_2\,Si\dot{C}H_2 \rightarrow [(CH_3)_3\,Si-O-Si\,(CH_3)_2-CH_2-]_2. \quad (III)$$

The formation of the higher-molecular-weight polymers proceeds either through removal of hydrogen atoms from low-molecular-weight polymers by interaction with $\dot{H}$ and $\dot{C}H_3$ or through splitting of isolated bonds in low-molecular-weight polymers under the direct influence of the electrical discharge. The resulting new radicals recombine to form higher-molecular-weight compounds.

The presence of octamethyltrisiloxane in the reaction products indicates that in addition to rupture of Si–C bonds in hexamethyldisiloxane, rupture of Si–O bonds also takes place to some extent:

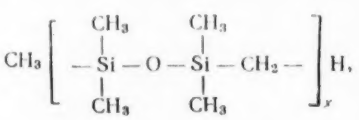
$$(CH_3)_3Si-O-\,Si\,(CH_3)_3 \rightarrow (CH_3)_3\,Si-\dot{O} + \dot{S}i\,(CH_3)_3.$$

The octamethyltrisiloxane probably results from recombination of the following two radicals:

$$(CH_3)_3Si-\dot{O} + \dot{S}i\,(CH_3)_2-O-\,Si\,(CH_3)_3 \rightarrow (CH_3)_3Si-O-Si\,(CH_3)_2-O-Si\,(CH_3)_3. \quad (I)$$

The C/Si ratio of 2.5-2.7 in the product compounds is somewhat lower than in the original hexamethyldisiloxane (C/Si of 3); an exception is compound III, for which this ratio is also equal to 3. As a rule, this ratio decreased somewhat with an increase in the molecular weight of the polymer. It follows from this that this polycondensation process is accompanied by partial, but not extensive, demethylation.

The elemental composition of V corresponds to a C/Si ratio of 2.5, which indicates that the high-molecular-weight polymers contained in V belong to the same type of heterochain linear polymers as II, III, and IV, and it also indicates that the polymers of this fraction contain alternating silane-hydrocarbon and siloxane units in their main chains. On this basis, the following formula may be proposed for the compounds of fraction V:



where x is 17.

Thus, this work has shown that polymeric organosilicon compounds, chiefly of low molecular weight and

containing alternating hydrocarbon-silane and siloxane units in the main chain, can be prepared in 50% yield by condensation of hexamethyldisiloxane under the influence of a sonic-frequency, high-voltage silent discharge in a flow system. This method can undoubtedly be used for the condensation of other organosiloxanes.

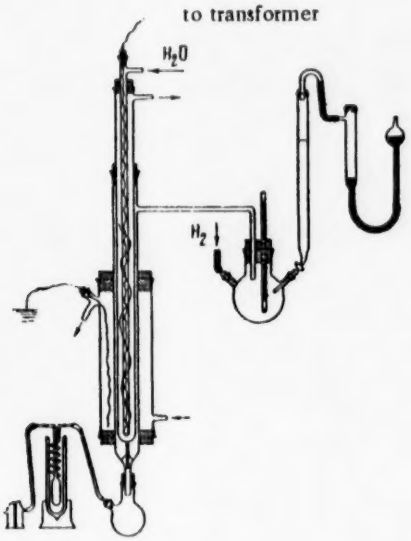


Fig. 1.

Experimental

The condensation experiments were carried out in the apparatus shown in Fig. 1. The reactor was constructed of No. 29 glass and had the following dimensions: internal diameter of the outer tube (outer electrode), 23.0± 0.05 mm; external diameter of the inner tube (inner electrode), 16.9 ± 0.05 mm; wall thickness of the tubes, 1.0-1.1 mm; distance between electrodes (width of the discharge gap), 3.05± 0.05 mm; length of the discharge zone, 300 mm; volume of discharge space, 57.0 cc. Both electrodes were cooled by flowing water. The inner electrode was connected to the high-voltage transformer, and the outer electrode was connected to ground. The current supplied to the transformer had a frequency of 4000 cps and was obtained from a converter.

The feed was passed from a graduated burette at a predetermined space rate into a flask fitted with an electric heater. Simultaneously, a flow of dry purified hydrogen was passed into the flask, and the mixture of hydrogen and vapor was passed through a side-arm into the upper part of the reactor. A slight excess pressure was maintained in the burette by means of a pear-shaped leveling bulb containing mercury. The hexamethyldisiloxane feed rate was 8-9 ml/hour, and the hydrogen feed rate was 5 liters/hour. The experiments were carried out with a voltage of 5 kv and a current of 4.5-5 ma in the secondary circuit. The gases leaving the reactor were passed through two traps, one cooled with solid carbon dioxide and the other with liquid nitrogen. Besides the original hexamethyldisiloxane, no other compounds were found in the traps. The original hexamethyldisiloxane had the following constants: b. p. 100-101°, n^{20}_D 1.3780, d^{20}_4 0.7620. A total of 570 g of hexamethyldisiloxane was passed into the reactor. After distillation of the unreacted siloxane there remained 287 g of condensation products in the form of a mobile yellow liquid. The yield was 51%.

The following individual compounds were obtained by fractionation of the condensation products:

Octamethyltrisiloxane (I) $(CH_3)_3Si-O-Si(CH_3)_2-O-Si(CH_3)_3$. B.p., 150-151° (757 mm); n^{20}_D 1.3847; d^{20}_4 0.8184. Molecular weight: found, 233; calculated, 236.5. MR_D: found, 67.67; calculated, 67.56.

Found %: C 40.44; Si 35.48; H 10.18
$C_8H_{24}O_2Si_3$. Calculated %: C 40.62; Si 35.63; H 10.23

Literature data [13]: b. p., 153°; n^{20}_D 1.3843; d^{20}_4 0.8200.

2,2,4,4,6,6,8,8-Octamethyl-2,4,6,8-tetrasila-3,7-dioxanonane (II) $(CH_3)_3Si-O-Si(CH_3)_2-CH_2-(CH_3)_2Si-O-Si(CH_3)_3$. B. p., 72-78 (3 mm); n^{20}_D 1.4119; d^{20}_4 0.8462. Molecular weight: found, 307; calculated, 308.7. MR_D: found, 90.75; calculated, 91.08.

Found %: C 42.52; Si 36.13; H 10.53
$C_{11}H_{32}O_2Si_4$. Calculated %: C 42.79; Si 36.40; H 10.45

Literature data [1]: b. p., 132-133° (54 mm); n^{20}_D 1.4121; d^{20}_4 0.8447.

2,2,4,4,7,7,9,9-Octamethyl-2,4,7,9-tetrasila-3,8-dioxadecane (III) $[(CH_3)_3Si-O-Si(CH_3)_2-CH_2-]_2$. B.p. 104-106° (4 mm); n^{20}_D 1.4190; d^{20}_4 0.8546. Molecular weight: found, 328; calculated, 322.7. MR_D: found, 95.37; calculated, 95.71.

Found %: C 44.82; Si 34.63; H 10.34
$C_{12}H_{34}O_2Si_4$. Calculated %: C 44.62; Si 34.80; H 10.62

2,2,4,4,6,6,8,8,10,10,12,12-Dodecamethyl-2,4,6,8,10,12-hexasila-3,7,11-trioxatridecane (IV) $[(CH_3)_3Si-O-Si(CH_3)_2-CH_2-Si(CH_3)_2-]_2O$. B. p., 135-140° (4 mm); $n^{20}D$ 1.4253; d^{20}_4 0.8770. Molecular weight: found, 460; calculated, 455. MR_D: found, 132.76; calculated, 133.44.

Found %: C 41.73; Si 36.54; H 10.30

$C_{16}H_{46}O_3Si_6$. Calculated %: C 42.23; Si 37.06; H 10.19

Literature data [1]: b. p., 184-185° (34 mm); $n^{20}D$ 1.4243; d^{20}_4 0.8725.

High boiling polymers with a b. p. above 280° (20 mm) (V). $n^{20}D$ 1.4606; d^{20}_4 0.9593. Molecular weight: found, 2476; calculated, 2504.

Found %: C 40.92; Si 38.12; H 9.86

$C_{86}H_{242}O_{17}Si_{34}$. Calculated %: C 41.25; Si 38.14; H 9.75

The elemental analyses were carried out in the microanalytical group of the Institute under the direction of Yu. N. Platonov.

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AMINATION OF POLYHALOGEN DERIVATIVES OF BENZENE

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The reactivity series F > Cl ~ Br[1]has been established for halogens in the reaction of aromatic halogen compounds with nucleophilic reagents by a bimolecular mechanism [1]. In the case of the reaction of aryl halides with amides of the alkali metals in liquid ammonia, which proceeds with the intermediate formation of dehydrobenzenes, the ease with which halogen is replaced by the amino group is precisely the reverse: F ≪ Cl < Br [2]. This same reactivity series of the halogens is observed during the amination of aromatic halogen compounds with aqueous ammonia in the presence of copper salts [3].

We felt that the interaction of aromatic halogen compounds with aqueous ammonia and with alkali metal amides in liquid ammonia could also proceed by a bimolecular mechanism. This would be possible during reaction with metal amides in cases in which the dehydrobenzene could not be formed. However, direct proof of this assumption is not available. Benkeser and Butting [4] explain the absence of reaction between 2-bromo-3-methoxytoluene and sodium amide in liquid ammonia by the impossibility of forming the corresponding dehydrobenzene derivative. It seems to us that this is a result of the low reactivity of bromine in nucleophilic substitution reactions proceeding by a bimolecular mechanism and also of steric hindrance.

The replacement of halogen by an amino group during the action of aqueous ammonia on aryl halides with an unactivated halogen atom will proceed by the usual bimolecular mechanism in the absence of copper salts. Such a mechanism for the replacement of a halogen atom by an amino group has previously been noted only for nitrohalobenzenes.

If these suppositions are correct, then the ease with which fluorine atoms are replaced by amino groups should be greater than that of other halogen atoms when either aminating agent is used. In order to confirm this latter assumption, we studied the interaction of hexahalobenzenes with potassium amide in liquid ammonia and the reaction of a number of polyhalogen derivatives of benzene with aqueous ammonia in the absence of copper salts. The experimental results are presented in Tables 1 and 2.

It is known that pentafluoroaniline is readily formed by the action of sodium amide in liquid ammonia on hexafluorobenzene at −70° [5]. The formation of pentachloroaniline occurs only when hexachlorobenzene is heated with aqueous ammonia (1 hour, 250°) [6].

It was not possible to separate the reaction products when hexabromobenzene and fluoropentabromobenzene were reacted with potassium amide. A comparison of the amounts of benzene split off and of the unreacted bromine derivative recovered indicated that 3-4 bromine atoms were simultaneously removed.

Our data show that fluorine atoms are replaced by amino groups at a greater rate than are chlorine and bromine atoms. This provides some degree of basis for our assumption that these reactions proceed by an ordinary bimolecular mechanism.

TABLE 1

Amination of Hexahalobenzenes by Potassium Amide in Liquid Ammonia (10 minutes)

Expt. No.	Starting compound	Halogen atom replaced			Separated from reaction mixture, % of compound charged	
		F	Cl	Br	amine	starting compound
1	C_6Cl_6	—	0,1	—	$C_6Cl_5NH_2$ 5	87
2	C_6Cl_5F	0,62	0,02	—	$C_6Cl_5NH_2$ 57	33
3	C_6Br_6	—	—	0,91	—	76
4	C_6Br_5F	0,16	—	0,82	—	65

TABLE 2

Amination of Polyhalobenzenes by Aqueous Ammonia

Starting compound	Reaction conditions		Halogen atom removed			Separated from reaction mixture, based on compound charged		
	Temp. °C	Reaction time, hr	F	Cl	Br	Amine	Amount, %	Starting compound, %
C_6Cl_6	200	1	—	0,13	—	$C_6Cl_5NH_2$	5	80
C_6Cl_5F	200	0,5	0,89	0,01	—	$C_6Cl_5NH_2$	79	3
C_6Cl_5F	200	1	1	0,03	—	$C_6Cl_5NH_2$	85	—
C_6Br_6	200	1	—	—	0,15	$C_6Br_5NH_2$	8	83
C_6Br_5F	200	1	0,79	—	0,09	$C_6Br_5NH_2$	65	15
m-C_6H_4ClF	250	6	0,41	0,06	—	m-$C_6H_4ClNH_2$	29	32

Experimental

1. To a solution of potassium amide, prepared in the usual manner [2] from 20 millimoles of metallic potassium and 100 ml of anhydrous liquid ammonia, was added 10 millimoles of finely ground hexahalobenzene. The mixture was stirred for 10 minutes, 1.7 g of NH_4NO_3 was added, and the ammonia was evaporated. The residue was treated with ether and filtered. The ether-insoluble precipitate was dissolved in water, and the amount of halogen split off was determined. The solvent was distilled from the ether solution, and the residue was treated at 50-60° with concentrated H_2SO_4, filtered from the undissolved hexahalobenzene, and the amine separated by pouring the filtrate into water.

TABLE 3

Compound	Formula	M.p., °C	Analytical results, %			
			found		calculated	
			nitrogen	halogen	nitrogen	halogen
Pentachloroaniline	$C_6Cl_5NH_2$	232 (232)	5,19 5,20	67,2 67,2	5,29	66,8
Diacetyl derivative	$C_{10}H_6Cl_5NO_2$	143,5	4,04 4,08		4,01	
Pentabromoaniline	$C_6Br_5NH_2$	262 (262)	2,80 2,72	81,9 81,6	2,87	81,9
Diacetyl derivative	$C_{10}H_6Br_5NO_2$	192,5	2,49 2,58		2,45	

* The melting point according to reference [7] is given in parentheses.

2. a) To a 200-ml rotating autoclave were charged 20 millimoles of hexahalobenzene and 150 ml of 30% aqueous ammonia. At the end of the reaction time, the reaction mixture was filtered, and the amount of halogen split off was determined in the filtrate. The precipitate was treated with H_2SO_4. Further treatment was as described above. b) A mixture of 2.93 g of m-fluorochlorobenzene and 150 ml of 30% aqueous ammonia was heated 6 hours at 250°. By a previously described method [3], 0.82g(29%) of m-chloroaniline was separated; b. p. 142°/68 mm, $n^{16.5}D$ 1.5945. A mixture of the acetyl derivative (m. p., 77.5°) with a known sample showed no depression of the melting point.

The diacetyl derivatives of the polyhaloanilines were prepared by boiling for several minutes 0.4 g of the amine with 5 ml of acetic anhydride in the presence of 2-3 drops of H_2SO_4 (1.84). The reaction mixture was poured into water and filtered. The products were recrystallized from alcohol. The properties of the products are presented in Table 3.

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*Original Russian pagination. See C. B. translation.

THE SYNTHESIS AND SOME REACTIONS OF 4-SUBSTITUTED THIOSEMICARBAZIDES

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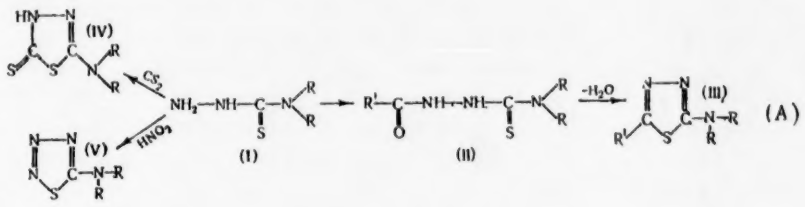
In planning our work on the synthesis of compounds which presumably have biological activity, we recalled the preparation of 4,4-di(β-hydroxyethyl) thiosemicarbazide (VII) and other 4,4-disubstituted thiosemicarbazides (I) and their subsequent conversion to azoles according to the scheme:



(A)

Of the compounds of interest to us, only 4,4-dimethyl- and 4,4-diethylthiosemicarbazides [1] and 5-dimethylamino-1,2,3,4-thiatriazole [2] have been described in the literature.

We confirmed that it is possible to prepare compound (VII) by the method of Jensen [1], which involves the preparation of dialkyldithiocarbamidoacetic acid and the interaction of its sodium salt with hydrazine hydrate. However, it was not possible to separate compound (VII) from the reaction mixture. At the same time, it was found that this reaction, after some simplification, can be successfully used for the preparation of 4-monosubstituted thiosemicarbazides. It was also found that these compounds can be prepared by successive treatment of the original amine with carbon bisulfide, sodium chloroacetate, and hydrazine hydrate, without separation of the intermediate products in accordance with:

$$R-NH_2 \xrightarrow[NH_4OH]{CS_2} R-NH-\underset{\underset{S}{\|}}{C}-SNH_4 \xrightarrow{ClCH_2COONa} \rightarrow R-NH-\underset{\underset{S}{\|}}{C}-SCH_2COONa \xrightarrow{NH_2-NH_2} NH_2-NH-\underset{\underset{S}{\|}}{C}-NH-R \qquad (B)$$

This method for the preparation of 4-monosubstituted thiosemicarbazides has the advantage of simplicity over the method of Pulvermacher [3], which has the disadvantage of requiring considerable expenditure of effort in synthesizing the isothiocyanates which are the starting materials for this method. By means of Scheme B, a series of 4-alkyl- and 4-arylthiosemicarbazides were prepared; these new compounds are described in Table 1.

Since we were unable to prepare 4,4-di(β-hydroxyethyl) thiosemicarbazides by the method of reference [1], we attempted to carry out the synthesis of this compound by another route:

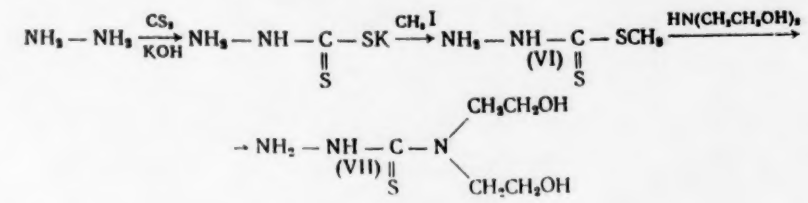


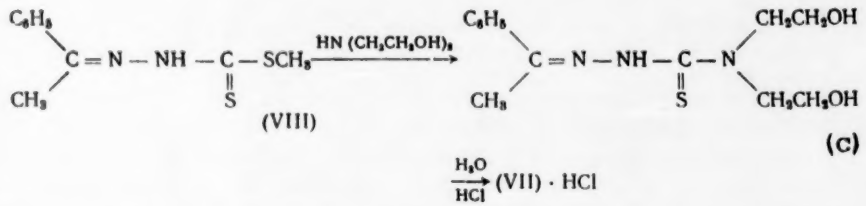
TABLE 1

4-Monosubstituted Thiosemicarbazides $NH_2-NH-C(=S)-NH-R$

R	M.p., °C	Yield %	Molecular formula	N, % found	N, % calc.	S, % found	S, % calc.
$-CH_2CH_2OH$	114–115	36	$C_3H_9ON_3S$	31.20	31.11	23.80	23.70
$-i-C_4H_{11}$	141–143	57	$C_5H_{13}N_3S$	24.22	24.27	18.52	18.49
$-CH_2CH_2-$	221 *	56	$C_4H_{10}N_6S_2$	40.35	40.38	30.75	30.76
$-(CH_2)_4-$	140–142 *	35	$C_5H_{11}N_3S_2$	32.30	31.81	24.18	24.24

* With decomposition.

As a matter of fact, as would be expected, the exchange of the thioester group of the methyl ester of dithiocarbazic acid (VI) for diethanolamine did take place, but it was accompanied by decomposition. For this reason, it was not possible to prepare compound (VII) by this method. In another attempt to carry out this reaction, we used in place of (VI) the products of its condensation with certain aldehydes and ketones, and we found that acetophenone methyldithiocarbazone (VIII) reacts smoothly with diethanolamine to give a good yield of acetophenone 4,4-di-(β-hydroxyethyl) thiosemicarbazone (IX). The latter was hydrolyzed with cold 1% HCl to yield the hydrochloride of compound (VII).



(VIII) (C)

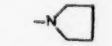
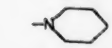
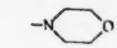
Compound VIII reacts just as well with other, sufficiently basic amines* as with diethanolamine giving the corresponding thiosemicarbazones (Table 2). The 4-(β-hydroxyethyl)- and 4,4-diethylthiosemicarbazides synthesized by Scheme C proved to be identical to those prepared by Scheme B; some previously undescribed thiosemicarbazides with cyclic radicals were also synthesized by Scheme C (Table 3).

Several of these 4,4-disubstituted thiosemicarbazides were converted to azoles by the method of Scheme A. These conversions were accomplished by means of reactions described as applicable to thiosemicarbazide and 4-monosubstituted thiosemicarbazides [4-8]. The 2-amino-5-alkyl(aryl) - 1,3,4-thiadiazoles substituted at the amino group (III) were prepared by ring closure in the intermediate acyl derivatives (II) with acetyl chloride or concentrated sulfuric acid. Compound (IV) was synthesized by refluxing (I) with carbon bisulfide in pyridine. The interaction of thiosemicarbazide hydrochlorides (I) with sodium nitrite gave substituted 5-amino-1,2,3,4-thiatriazoles (V). Some of the compounds synthesized by Scheme A are described in Table 4.

* Aromatic amines did not react with compound (VIII) under similar conditions.

TABLE 2

4-Substituted Acetophenone Thiosemicarbazones $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!C=N-NH-\underset{\underset{S}{\|}}{C}-R$

R	M.p., °C	Yield, %	Molecular formula	N, % found	N, % calc.	S, % found	S, % calc.
$-NH-CH_2CH_2OH$	108—109	97	$C_{11}H_{15}ON_3S$	17,50	17,72	—	—
$-N(CH_2CH_2OH)(CH_2CH_2OH)$	133—135	95	$C_{15}H_{19}O_3N_3S$ •	14,86	14,94	11,71	11,38
	134—135	90	$C_{13}H_{17}N_3S$	16,99	17,00	13,01	12,96
	101—102	96	$C_{14}H_{19}N_3S$	15,55	16,09	12,03	12,26
	105—107	98	$C_{13}H_{17}ON_3S$	15,69	15,96	12,41	12,16

• Calculated %: C 55.51; H 6.76. Found %: C 55.26; H 6.60.

TABLE 3

4,4-Disubstituted Thiosemicarbazides $NH_2-NH-\underset{\underset{S}{\|}}{C}-R$

R	M.p., °C	Base: Molecular formula	Base: N, % found	Base: N, % calc.	Base: S, % found	Base: S, % calc.	Hydrochloride: hydrochloride m.p. (with decomp.), °C	Hydrochloride: Yield, %	Hydrochloride: N, % found	Hydrochloride: N, % calc.
$-N(CH_2CH_2OH)(CH_2CH_2OH)$	—	$C_7H_{17}O_2N_3S$	—	—	—	—	149—151	67	19,64	19,48
	163—165 (with decomp.)	$C_6H_{13}N_3S$	28,48	28,96	22,12	22,06	206—208	98	22,92	23,14
	95—96,5	$C_7H_{15}N_3S$	26,12	26,41	19,96	20,12	200—202	76	21,31	21,48
	176—177 (with decomp.)	$C_6H_{11}ON_3S$	26,18	26,08	19,81	19,87	164—166	70	21,39	21,26

Experimental

Acetophenone methyldithiocarbazone (VIII). To 12.2 g (0.1 mole) of the methyl ester of dithiocarbazic acid [9] in 100 ml of alcohol was added 12 g (0.1 mole) of acetophenone, and the mixture was refluxed for 10 minutes. There was obtained 21 g (94%) of yellow prisms with an m. p. of 142-143° (from alcohol). Found, %: N, 12.49. Calculated for $C_{10}H_{12}N_2S_2$, %: N, 12.50.

Acetophenone 4,4-di(β-hydroxethyl) thiosemicarbazone (IX). A mixture of 18 g (0.08 mole) of (VIII) and 10.5 g (0.1 mole) of diethanolamine in 100 ml of methyl alcohol was refluxed for 9 hours. The reaction mixture was allowed to cool, and was then diluted with water until the further addition of water caused no increase in the turbidity. After standing for 2 hours, the mixture was filtered, and 20 g (90%) of light yellow needles were obtained. These crystals were recrystallized from 50% methyl alcohol.

The remaining 4-substituted acetophenone thiosemicarbazones were prepared under similar conditions (Table 2).

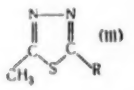
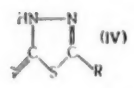
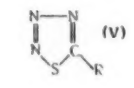
4,4-(β-Hydroxyethyl) thiosemicarbazide hydrochloride. The (IX), 28.1 g (0.01 mole), was extracted for 3

hours with 300 ml of cold dilute hydrochloric acid containing 0.09 mole of HCl. The acetophenone formed during the hydrolysis was extracted with ether, and the excess (IX) was separated. The filtrate was evaporated to a viscous mass, which crystallized when stored in a vacuum desiccator over silica gel. The crystals were ground with anhydrous alcohol, filtered, and reprecipitated from alcohol by the addition of ether.

The other acetophenone 4-substituted thiosemicarbazides were hydrolyzed under more vigorous conditions, i. e., with 3-4% hydrochloric acid and heating on a water bath. The free bases were separated with sodium acetate. The new 4,4-disubstituted thiosemicarbazides and their hydrochlorides are described in Table 3.

TABLE 4

Substituted 2-Amino-5-methyl-1,3,4-thiadiazoles (III), 2-Amino-1,3,4-thiadiazoline-5-thiones (IV), and 5-Amino-1,2,3,4-thiatriazoles (V)

Structure	R	M.p., °C	Yield, %	Molecular formula	N, % found	N, % calc.	S, % found	S, % calc.
 (III)	$-N(CH_3)_2$	186–188 **	80	$C_6H_{11}N_3S \cdot HCl$	23,52	23,39	17,74	17,82
		43–44,5	88	$C_9H_{13}N_3S$	22,72	22,95	17,67	17,48
		88–90	71	$C_7H_{11}ON_3S$	22,82	22,70	17,49	17,30
 (IV)	$-N(CH_3)_2$	174–175	34	$C_6H_{11}N_3S_2$	26,06	26,09	39,69	39,75
		165–167	72	$C_9H_{13}N_3S_2$	20,97	20,89	32,13	31,84
		173–175	25	$C_7H_{11}ON_3S_2$	20,73	20,68	31,24	31,52
 (V)	$-N(CH_3)_2$	48–50 * (49–51)	35	$C_5H_9N_4S$	—	—	—	—
		28–29	65	$C_9H_{11}N_4S$	32,71	32,94	19,04	18,82
		114–115	87	$C_7H_9ON_4S$	32,31	32,55	18,74	18,60

* Characterized in the form of the hydrochloride.

** With decomposition.

2-(N-piperidyl)-5-methyl-1,3,4-thiadiazole. To 2 g (0.01 mole) of 1-acetyl-4,4-pentamethylenesemicarbazide, prepared by acetylation with acetic anhydride in the cold, was added 5 ml (0.06 mole) of acetyl chloride. After an hour, the mixture was carefully made alkaline with 30% NaOH. The amine was extracted with ether, and was purified by reprecipitation from ether by the addition of petroleum ether. The amine was readily soluble in water and organic solvents.

2-(N-Piperidyl)-1,3,4-thiadiazoline-5-thione. To 1.95 g (0.01 mole) of 4,4-pentamethylenesemicarbazide in 15 ml of pyridine was added 0.9 ml (0.015 mole) of carbon bisulfide, and the mixture was refluxed for 4 hours; the mixture was then allowed to cool, and was poured into 100 ml of 2 N HCl. The product which separated was recrystallized from 50% methyl alcohol.

5-(N-Piperidyl)-1,2,3,4-thiatriazole. To 1.95 g (0.01 mole) of 4,4-pentamethylenesemicarbazide hydrochloride in 10 ml of water, which was cooled to 0°, was added dropwise a solution of 0.7 g (0.01 mole) of sodium nitrite in 10 ml of water. The resulting substance was recrystallized from petroleum ether.

All of the remaining compounds described in Table 4 were prepared in a manner similar to the last three.

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ON THE MECHANISM OF THE FORMATION OF ETHYLENE IN ISOBUTYLENE CRACKING

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The study of the mechanism of thermal cracking of olefins (T = 500-700°C) is considerably complicated by the occurrence of polymerization reactions. The further conversion of the products of these reactions can significantly distort the spectra of the primary products. Ordinarily, the primary products are determined by extrapolating the mole fractions of the individual products to zero percent conversion. However, it has not previously been evident that this method can be unconditionally used in such complex systems.

Hurd and Eilers [1] studied isobutylene cracking in a flow system. Using the extrapolation method, they found that methane, ethylene, and propylene are primary cracking products. In a study of the thermal cracking of isobutylene under static conditions [2], we also found, by means of the extrapolation method, that in addition to methane, propylene, isobutane and hydrogen, ethylene is a primary cracking product.

However, the structure of the isobutylene molecule is such that it is very difficult to imagine how the ethylene molecule is formed either directly from the isobutylene or from the radical $CH_2{:}CH(CH_3)\dot{C}H_2$. This circumstance forced Hurd and Eilers to the conclusion that the application of the extrapolation method to ethylene leads to incorrect results and that the ethylene is wholly formed from propylene during isobutylene cracking.

In work reported in reference [3], we studied the thermal decomposition of isobutylene with labeled (C^{14}) propylene added to the feed, and it was shown that only an insignificant part of the ethylene was formed from the propylene. In this same work, we established that in this reaction propylene is formed not only directly from the isobutylene, but also as a result of decomposition of products of the polymerization of isobutylene. It was natural to assume that ethylene could also be formed by this same route.

In order to obtain a final answer to the question of ethylene formation, we studied isobutylene cracking with the addition of labeled ethylene* to the charge. Labeled ethylene was added to the isobutylene in a concentration of 0.2%, and 300 ml of the mixture was cracked at a temperature of 545°.

The cracked products were separated in a column filled with ASM silica gel. To the resulting ethylene was added unlabeled ethylene, and the mixture was oxidized to CO_2 over CuO in a stream of nitrogen. The CO_2 was absorbed in $Ba(OH)_2$, and the activity of the precipitated $BaCO_3$ was measured with an end-window counter.

Figure 1 shows the change in the concentration (a) and the change in the specific activity (b) of ethylene during cracking.

The rate of formation of ethylene was calculated by the equation [4]:

$$w = -2.3\,[C_2H_4]\frac{d\log\alpha}{dt}.$$

*The labeled ethylene was kindly presented to us by the laboratory of tagged atoms, M. B. Neiman director.

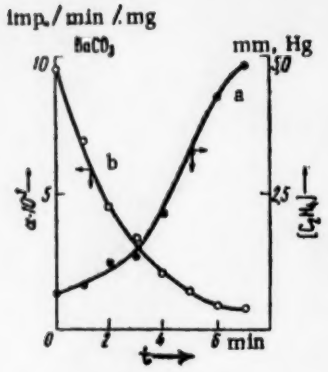


Fig. 1.

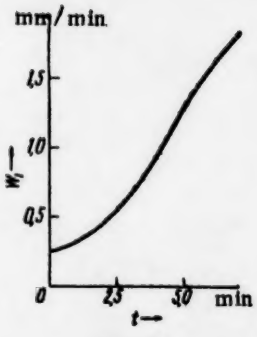
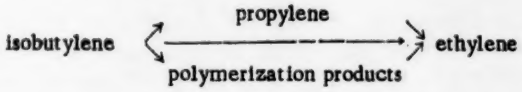


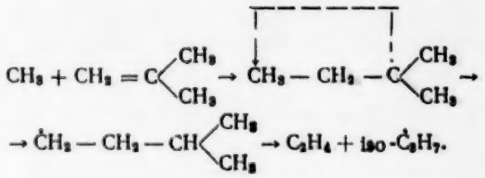
Fig. 2.

Figure 2 shows the dependence of the rate of ethylene formation on time. The rate was not equal to zero at time zero, whence, it follows that part of the ethylene was formed directly from the isobutylene.

The routes by which ethylene is formed during thermal cracking of isobutylene may be schematically represented as:



As regards the mechanism of the formation of ethylene directly from isobutylene, this may be represented as follows:



Methyl radicals are undoubtedly present in the reaction zone. Unfortunately, there are no experimental data from which it may be sufficiently reliably concluded that radical isomerization actually takes place under the conditions existing during cracking of hydrocarbons.

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*Original Russian pagination. See C. B. translation.

THE ADDITION OF DIALKYL PHOSPHITES TO 1,5-NAPHTHALENE DIISOCYANATE

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(Presented by Academician B. A. Arbuzov, May 23, 1960)
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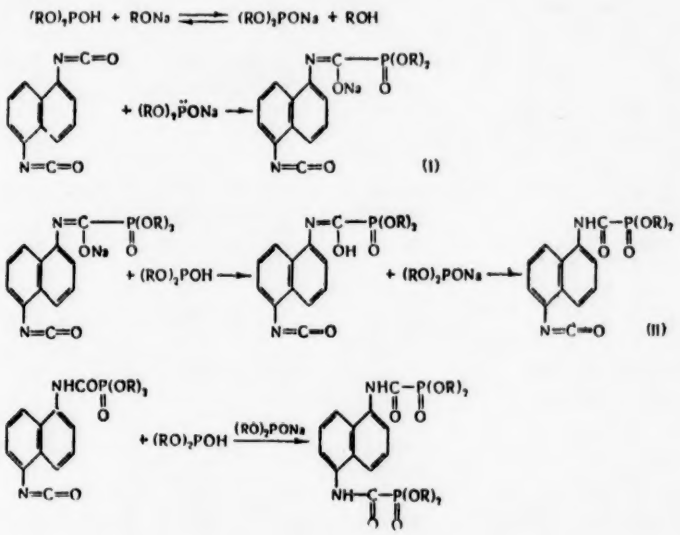
pp. 830-832, October, 1960
Original article submitted May 17, 1960

It is known that dialkyl phosphites readily add to substances containing carbon–oxygen, carbon–nitrogen, and unsaturated carbon–carbon bonds with the formation of various phosphorus-containing compounds.

The reaction of dialkyl phosphites with esters of isocyanic acid [1-3] yields dialkyl esters of amidophosphonoformic acid [dialkylcarbamoylphosphonates].

It was of interest, therefore, to study the addition of dialkyl phosphites to diisocyanates. In the present work, it was shown that dialkylphosphites readily add to 1,5-naphthalene diisocyanate. The addition reaction can be represented as follows:



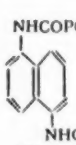
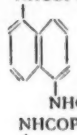
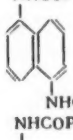
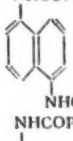
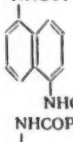
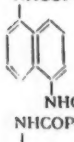
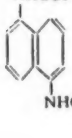
Where R = CH_3; C_2H_5; n-C_3H_7; iso-C_3H_7; n-C_4H_9; iso-C_4H_9, iso-C_5H_{11}; $CH_2=CH-CH_2$.

A possible mechanism for this conversion involves an exchange reaction between the initial sodium alcoholate and the dialkyl phosphite. The resulting dialkyl sodium phosphite in the enol form then reacts with a carbonyl

group of one of the isocyanate groups of the diisocyanate molecule. Intermediate product I is thus formed initially. This product reacts with the dialkyl phosphite with the formation of product II, 5-naphthaleneisocyanate-1-dialkyl ester of amidophosphonoformic acid [1-dialkylphosphonoformamido-5-isocyanatonaphthalene].

The second NCO group then reacts by this same scheme with the formation of naphthalene-1,5-bisdialkyl ester of amidophosphonoformic acid [1,5-bis(dialkylphosphonoformamido) naphthalene]. The reaction takes place when the reactants are heated in a medium of chlorobenzene for a short time on a water bath. The addition products are white crystalline substances, soluble in alcohol, acetone, dioxane, etc. The properties of these products are presented in Table 1.

TABLE 1

Formula	Recrystallization solvent	M.p., °C	Phosphorus content, %		Yield, %
			found	calc.	
	Acetone	185 with decomp.	14,7	14,4	80
	acetone, alcohol	186—187 with decomp.	12,77	12,76	85,7
	acetone, alcohol	186 with decomp.	11,32	11,65	87
	acetone, alcohol	184—185 with decomp.	11,37	11,65	85
	alcohol, dioxane	183—184 with decomp.	9,8	10,36	84
	alcohol, dioxane	180—181	10,36	10,36	89
	alcohol, acetone	174—175	8,96	9,48	90
	alcohol	157—159	11,14	11,6	95

For proof of the structure of these addition products, one on them—naphthalene-1,5-bis-di-n-butyl ester of amidophosphonoformic acid—was prepared by the method of A. E. Arbuzov from naphthalene-1,5-bis(carbamoyl) chloride and tri-n-butyl phosphite. A mixed sample of the two compounds melted without depression of the melting point.

It has thus been found that the reaction of dialkyl phosphites with diisocyanates proceeds readily.

We acknowledge with appreciation the assistance of T. P. Veselova in the experimental work.

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*Original Russian pagination. See C.B. translation.

THE MASS SPECTRA AND STRUCTURES OF SILICON-CONTAINING VINYLACETYLENES

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(Presented by Academician B. A. Arbuzov, June 6, 1960)
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Original article submitted May 20, 1960

An investigation of the mass spectra of vinylacetylene and its homologs permitted us to establish the relationship between peak intensities of molecule-and certain fragment ions and the structures of the hydrocarbons [1].

In the spectra of vinylacetylene and its closest homologs, the highest intensities were due to the molecule-ions. With an increase in the size of the alkyl radicals there was a sharp drop in the intensity of the the molecule-ions and an increase in the intensity of the fragment ions, and among the latter, the ion of mass 39 is deserving of attention. Two maxima were observed for the ions $C_3H_X^+$ and $C_6H_X^+$ in the spectra of all enyne hydrocarbons which did not contain a tert-butyl radical. Enyne hydrocarbons containing a tert-butyl radical decomposed differently under electron impact. If such a hydrocarbon decomposed at a double bond beta to the triple bond, there was a high peak due to the ion $C_4H_9^+$ with mass 57. When the tert-butyl radical was located at the triple bond, it was not split off. In this case, the molecule-ion decomposed mainly by successive splitting off of methyl groups.

In the light of these data, it was unquestionably of interest to study the mass spectra of silicon-containing enyne hydrocarbons. We investigated the mass spectra of four silicon-containing enyne hydrocarbons: 1-trimethylsilyl-3-buten-1-yne (I), 1-trimethylsilyl-3-methyl-3-buten-1-yne (II), 1-trimethylsilyl-3-penten-1-yne (III), and 1-triethylsilyl-3-buten-1-yne (IV).

In contrast to the vinylacetylenic hydrocarbons, the dissociative ionization of their silicon-containing analogs was remarkably selective (Table 1).

Under the effect of electron impact the trimethylsilylbutenyne molecule (I) underwent decomposition predominantly with cleavage of a single methyl radical; the molecule-ion of mass 124 had a low peak, while the ion of mass 109 formed 48% of the total ion current.

$$[(CH_3)_3\,Si{-}C{\equiv}C{-}CH{=}\,CH_2]^+ \rightarrow (CH_3)_2\,Si^+{-}C{\equiv}C{-}CH{-}CH_2$$
$$124\ (13.5\%) \qquad\qquad 109\ (100\%)$$

Further decomposition took place with the formation of silicon-containing ions with masses of 93, 83, 81, 79, 69, and 55 with intensities of from 3 to 15%; the process proceeded by successive cleavage of CH, CH_2, or CH_3 groups. There was no doubt as to the presence of silicon in these ions, since the spectrum of each contained the characteristic grouping of peaks associated with the presence of the three silicon isotopes.

The decomposition of the two closest homologs of (I), the silicon-containing hydrocarbons (II) and (III), was similar; for both homologs, the most abundant ion was mass 123, which was formed by cleavage of a methyl group from the molecule-ion:

$$[(CH_3)_3Si-C\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2]^+ \rightarrow (CH_3)_2Si^+-C\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2$$

138 (7,8%) 123 (100%)

$$[(CH_3)_3Si-C\equiv C-CH=CH-CH_3]^+ \rightarrow (CH_3)_2Si^+-C\equiv C-CH=CH-CH_3$$

138 (5,4%) 123 (100%)

Further decomposition of (II) and (III) was less than in the case of (I); the ion with mass 123 comprised 68-71% of the total ions.

The most abundant ion in the spectrum of the saturated analog of (I)—trimethylbutylsilane—was the ion $(CH_3)_3Si^+$ with a mass of 73. There was considerably less decomposition by cleavage of methyl groups; this course of decomposition was apparent in the spectrum by the presence of a peak for the $(CH_3)_2Si^+H$ ion with a mass of 59. The peaks due to the remaining ions were low.

TABLE 1

Mass Spectra of Enyne Silanes*

Ion mass	(I)	(II)	(III)	(IV)	Ion mass	(I)	(II)	(III)	(IV)
15	1,1	—	—	—	80	—	—	—	6,6
26	—	—	—	2,6	81	3,5	—	—	79,7
27	—	—	—	7,4	82	—	—	—	7,9
28	2,7	—	—	8,3	83	7,7	1,8	2,2	5,6
29	—	—	1,2	6,1	93	2,9	1,9	1,0	2,4
39	1,1	—	—	2,0	95	1,0	—	2,0	2,4
41	—	—	—	5,3	97	—	3,2	—	—
42	1,1	—	—	—	107	1,0	1,1	—	4,4
43	15,1	—	—	10,4	108	—	—	—	1,9
44	3,3	—	6,5	4,3	109	100,0	—	—	100,0
45	1,7	1,2	—	—	110	3,8	—	—	11,5
46	—	—	1,3	—	111	—	—	—	3,8
53	10,7	3,24	3,4	18,3	121	—	5,3	—	—
54	1,3	—	—	5,5	122	—	5,6	—	—
55	5,4	1,8	1,2	18,4	123	—	100,0	100,0	—
56	—	—	—	1,9	124	13,5	—	3,6	—
57	—	—	—	5,5	125	1,1	—	—	—
66	2,7	1,2	—	1,4	137	—	—	—	74,9
67	6,6	4,5	2,7	4,9	138	—	7,8	5,4	7,8
69	14,0	2,4	3,1	13,7	139	—	—	—	2,8
77	2,6	—	—	3,0	166	—	—	—	8,0
79	6,4	—	—	20,2					

* Ion peaks with intensities less than 1% are not reported in the table.

The mass spectrum of triethylsilylbutenyne (IV) was characterized by peaks resulting from deeper decomposition of the molecule-ion. The greatest intensities in this spectrum belonged to ions with masses of 137, 109, and 81.

The major course of the dissociative ionization process of (IV) may be represented by the following scheme:

$$[(C_2H_5)_3Si-C\equiv C-CH=CH_2]^+ \rightarrow (C_2H_5)_2Si^+-C\equiv C-CH=CH_2 \rightarrow$$

166 (8%) 137 (74,9%)

$$\rightarrow C_2H_5-\underset{\underset{H}{|}}{Si^+}-C\equiv C-CH-CH_2 \rightarrow H_2Si^+-C\equiv C-CH=CH_2$$

109 (100%) 81 (79,7%)

Ions of mass 166, 137, 109, and 81 constituted 55% of the total ion current.

As the scheme shows, the initial stage in the dissociation of all silicon-containing vinylacetylenes is the same; this stage is the cleavage of an alkyl radical from the silicon atom. In the case of (IV), subsequent decomposition is by removal of successive ethylene molecules.

The correctness of this scheme for the decomposition of (IV) is confirmed by the presence in the spectrum of peaks associated with the corresponding metastable ions. It is well known that the presence of the latter is proof of specific stages of a decomposition process.

The decomposition $C_8H_{13}Si^+ \rightarrow C_6H_9Si^+$ should be accompanied by the formation of a metastable ion with a fractional mass, 86.7 ($m_A = \frac{m^2}{m_1}$) [6], and as a matter of fact, there was present in the spectrum a peak at 86.7 with an intensity of 1.3% of the maximum.

The decomposition $C_6H_9Si^+ \rightarrow C_4H_5Si^+$ was responsible for the presence in the spectrum of an ion of mass 60.1 and an intensity of 0.7%.

It is interesting that during the decomposition of (IV) there was formed an ion with a mass of 109; this ion was apparently isomeric with the ion of the same mass which arose during the dissociation of (I). The conversions observed during the interaction of silicon-containing enynes with electrons bear a specific similarity to certain chemical reactions of tetraalkylsilanes. Trialkylsilanes and olefins are observed during thermal cracking of tetraalkylsilanes [3, 4]. A single methyl group is split off by the action of sulfuric acid on organosilicon compounds containing the $(CH_3)_3Si$ group [5].

A comparison of the mass spectra of enyne hydrocarbons with those of their silicon-containing analogs allowed us to establish certain analogies and differences connected with the substitution of silicon for carbon.

Tert-butyl and trimethylsilyl radicals at a triple bond behave similarly; they are not split off as such, nor does decomposition by removal of a methyl group occur. However, in the case of the silicon-containing hydrocarbons, decomposition occurs primarily by removal of one methyl group, and the ions appearing in the spectra with the greatest intensity are those which are formed with accompaning migration of hydrogen. In the case of enyne hydrocarbons of analogous structure, the demethylation process is not limited to a single methyl group; the process continues and is accompanied by dehydrogenation with the formation of the ion $C_7H_7^+$, which apparently has the structure of the tropylium ion [6].

If the molecule does not contain multiple bonds (for example, trimethylbutylsilane and 2,2-dimethylhexane), processes in which trimethylsilyl and tert-butyl radicals are split off occur.

All of the trialkylsilylalkenynes investigated were prepared from trialkylchlorosilanes and vinylacetylenylmagnesium bromides by M. D. Stadnichuk, to whom the authors express their thanks.

The investigation was carried out with an MS-1 apparatus fitted with previously described refinements.

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*Original Russian pagination. See C.B. translation.

CHEMISORPTION OF ISOPENTANE ON CHROMIA–ALUMINA–POTASSIUM CATALYST

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pp. 836-839, 1960
Original article submitted May 12, 1960

Numerous investigations have been devoted to the various aspects of the problem of the dehydrogenation of paraffinic hydrocarbons; these have recently been reviewed by Lyubarskii [1]. Among the catalysts which have been used for this purpose, chromia-alumina catalysts, particularly those promoted with potassium [2-4], occupy first place. Results of investigations of the phase composition, texture, and other physical properties of unpromoted chromia-alumina catalysts have been described in references [5-8], and similar investigations of catalysts promoted with K_2O have been reported in reference [9]. Not only N_2, but other adsorbates also – CH_3OH [10], benzene [6, 9], toluene [6] – have been used in investigating the structure of catalysts; however, chemisorption was neither observed nor studied in any of these investigations. In one of the investigations [11] of adsorption on Cr_2O_3–MnO, chemisorption of CH_4, C_2H_6, and C_3H_8 was observed above 300°, but it was not studied in detail. These references exhaust the literature on the chemisorption of paraffins. The literature does contain indications that high-temperature chemisorption of hydrocarbons on oxides proceeds reversibly by a dissociation mechanism and with a low activation energy. Moreover, it has been proposed [14, 6] that the slow stage in catalytic conversions of hydrocarbons is chemisorption. In the light of the above, it seemed important to attempt to detect and to study in greater detail the chemisorption of paraffins and olefins at temperatures as close as possible to temperatures used in the dehydrogenation of paraffins. The present communication describes the results of a study of the adsorption of iso-C_5H_{12} on a standard paraffin dehydrogenation catalyst, which was kindly given to us by the authors of reference [4].

The texture of this catalyst, which contained 84.6 wt. % Al_2O_3, 13% Cr_2O_3, and 2.4% K_2O, was determined (with the assistance of A. L. Klyachko-Gurvich) by adsorption of benzene vapor at 20° in an apparatus with a quartz McBain balance. The surface area, S, was 120 sq m/g, and the effective pore diameter was of the order of 40 A. A determination carried out with argon gave a value of S of 135 sq m/g, which is in good agreement with the value determined with benzene vapor.

The adsorption of isopentane was studied by the capillary method described in reference [15]. The quantity of adsorbed isopentane (with correction for the amount in the dead space of the apparatus) was measured with an accuracy of 0.001 mmole. The isotherms were obtained at 20, 50, 100 and 150° (Fig. 1) and at 205, 241, 297, and 325° (Fig. 2), and were easily reproduced in repeated independent measurements. The catalyst was evacuated at 470-500° to a pressure of the order of $1 \cdot 10^{-4}$ prior to each series of experiments. With an increase in the temperature from 20 to 150°, the amount of iso-C_5H_{12} adsorbed at the same pressure decreased and the form of the isotherm changed. The isotherm at 20° was of the type associated with polymolecular adsorption. BET calculations using the data of this isotherm showed that 3.02 μmoles of iso-C_5H_{12} covered 1 square meter of surface at monolayer coverage and that the surface occupied by 1 molecule of iso-C_5H_{12} was 56 square angstroms.

However, at 100-150° and pressures of from 0 to 200 mm, the process took place in the region of low surface coverage (the region in which Henry's law holds) in which adsorption depends linearly on pressure, $a = k \cdot p$, and the isotherm was a straight line passing through the origin. Such an isotherm is one of the criteria of homogeneity of the catalyst surface with respect to physical adsorption. Since another necessary criterion of such homogeneity of surface is independence of the heat of adsorption, Q, of the degree of surface coverage, θ, it was desirable to check this variation. With this aim, calculations of the isosteric heat of adsorption of iso-C_5H_{12} on this catalyst (Table 1) were made using the Clausius-Clapeyron equation $d \ln P/dT = Q/RT^2$. The heat of adsorption changed very little with an increase in θ from 6 to 66% of a monolayer, which confirms that the surface was close to homogeneous. The very slight decrease in Q may have been associated with interaction of the iso-C_5H_{12} molecules with each other. The heat of adsorption determined at low surface coverage from the isotherms at 150, 205, and 241° also remained constant, but the value was lower than that obtained from isotherms at 20 and 50° by extrapolation. Similar deviations have been described in the literature for other cases, and were explained [16] primarily by the fact that with an increase in temperature the distance between an adsorbed molecule and the surface of the catalyst increases somewhat.

TABLE 1

a, μmoles/sq m	2	1.5	1.0	0.5	0.2	0.075	0.050	0.025
θ, %	66	49	33	16	6			
Q, kcal/mole	9.6	9.9	10.4	10.5	10.7	7.5	7.2	7.5

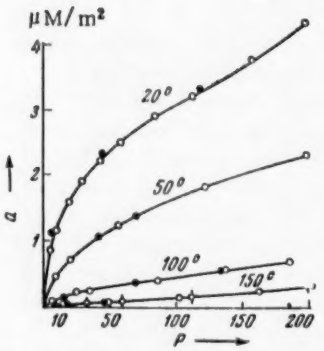

Fig. 1. Adsorption isotherms for isopentane on chromia–alumina–potassium paraffin dehydrogenation catalyst. Solid points represent desorption.

Above 150° and in the initial part of the isotherm, up to a pressure of 10-15 mm, there was an increase in the amount of adsorbed material with an increase in temperature. The isotherm changed from a linear and reversible type to a concave and irreversible type (205-325° Fig. 2), a Langmuir type isotherm reaching saturation. Adsorption was very slow in this region. Our isotherms show that between 150 and 205° there is another type of interaction between the iso-C_5H_{12} and the catalyst surface which is concluded at a pressure of 10-15 mm. Above these pressures, the isotherms continue to be linear and reversible, equilibrium is established rapidly in these regions, and adsorption drops with increasing temperature. Decomposition of isopentane on the catalyst with desorption of the reaction products does not take place at temperatures up to 300°, as may be seen from the isotherm at 297°, for example, the desorption branch of which shows that a significant amount of isopentane is chemisorbed. Although chemisorption also occurs at 325°, and even to a greater extent than at 297°, the desorption branch of the isotherm could not be determined accurately, since the iso-C_5H_{12} decomposed during the long contact with the catalyst at these temperatures and pressures, and the reaction products were desorbed from the catalyst. From the fact that the 325° isotherm retained a linear form at higher pressures, it follows that an insignificant amount of iso-C_5H_{12} underwent reaction at this temperature. It was generally not possible to obtain an isotherm at 350°, since there was considerable reaction as shown by the increase in pressure in the system; iso-C_5H_{12} conversion products were collected during this experiment. Analysis of these products (by Yu. A. Fedyunin, to whom we express our appreciation) with MI-1035 mass spectrometer showed that they comprised (in vol. %) C_3H_8, 28; CH_4, 25.6; C_2H_6, 16.7; C_2H_4, 8; C_3H_6, 6.2; C_2H_2, 3.7; C_4H_{10}, 2.8; C_5H_{10}, 2.6; benzene, 2.6; toluene, 1.34. Thus, owing to the very long contact with the catalyst at 350° under the static conditions of the experiment, the isopentane decomposed completely, and not only cracking but a series of consecutive reactions occurred including some leading to the formation of small amounts of aromatic hydrocarbons. Hence, there is an essential distinction between the behavior of isopentane under the conditions described above and its behavior in a flow system. It is well known [2-4] that dehydrogenation is the basic process when paraffins are contacted with this type of catalyst in a flow system at 500-550° and low contact times.

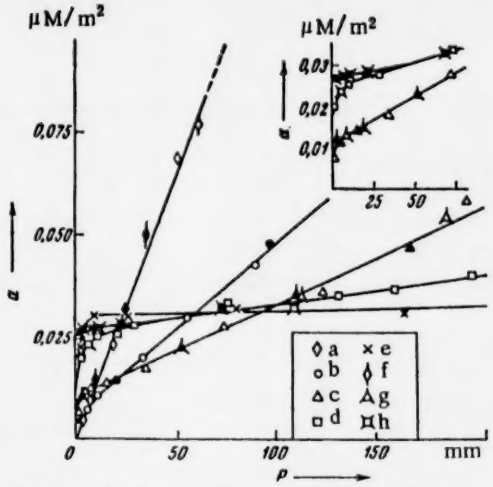

Fig. 2. Adsorption isotherms for isopentane on chromia–alumina–potassium catalyst at 150-325° (the initial parts of the 297 and 241° isotherms are shown separately on an enlarged scale). a) 150°, b) 205°, c) 241°, d) 297°, e) 325°, f to h) control experiments. Solid points represent desorption.

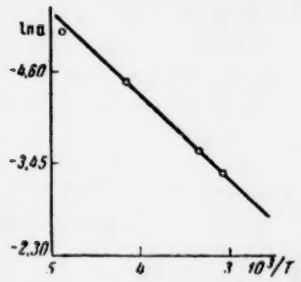

Fig. 3. Variation of the amount of isopentane chemisorbed on chromia–alumina–potassium catalyst with temperature.

The amount of chemisorbed isopentane varied exponentially with temperature (Fig. 3). At 241, 297, and 325° it amounted to, respectively, 0.33%, 0.9%, and 1.2% of the amount of isopentane adsorbed in a monolayer on the surface of the catalyst at 20°. The linear dependence of the logarithm of the amount of chemisorbed isopentane on the reciprocal of the temperature (Fig. 3) can be explained both by an increase in the number of chemisorption centers on the catalyst surface with an increase in temperature and by an increase in the reactivity of the isopentane itself with an increase in temperature. It is most probable that both of these factors act simultaneously.

We were unable to obtain reliable data on the rate of chemisorption of iso-C_5H_{12}, since the experiments were carried out without circulation of isopentane vapors and in a closed system, the different parts of which were at different temperatures (the tube containing the catalyst was at a higher temperature than the remainder of the apparatus). Nevertheless, these rates can be evaluated approximately from the amount of isopentane chemisorbed at the time equilibrium was established. Thus, a = 0.036 mmole (on the entire catalyst) was reached in 96 hours at 297° and in 31 hours at 325°. Since we had at our disposal data for two temperatures at the same value of θ, we were able to calculate (though only approximately, as indicated above) the activation energy for chemisorption of isopentane on this catalyst. The value was 15 kcal/mole.

Thus, in the present investigation we have, for the first time, measured the chemisorption of a paraffin hydrocarbon on a dehydrogenation-dehydrocyclization catalyst, determined its variation with temperature and pressure, and also approximately evaluated the activation energy of chemisorption. It follows from the data that the rate of chemisorption of isopentane increases rather rapidly with temperature, and, consequently, must be rather high at the temperatures employed in paraffin dehydrogenation (500° and higher). From the rapid increase in the number of chemisorption centers (evaluated from the increase in the amount of chemisorbed isopentane) with temperature, it follows that a significant fraction of the catalyst surface must take part in chemisorption at 500-550°. In fact, calculation by extrapolation of the graph of Fig. 3 to 550° shows that about 18.8% of the surface, as calculated from monolayer adsorption at 20°, must be capable of isopentane chemisorption at this temperature. Assuming that isopentane present by virtue of activated adsorption undergoes reaction, it can be calculated that about two tenths of the entire surface takes part in the dehydrogenation reaction at 550°. At the present time, we are studying chemisorption of isopentenes on this same catalyst.

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THE TEMPERATURE DEPENDENCE OF THE SURFACE TENSION OF GALLIUM

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The surface tension of gallium (σ) was first measured by Richards and Boyer [1], who found by the sessile drop method that σ for gallium at 30° C is 358.2 dynes/cm. Frumkin and Gorodetskaya [2] later indicated that this value is too low, and they determined it at the interface with an electrolytic solution from the maximum in electrocapillary curves, obtaining a value of 592 dynes/cm. Using the sessile drop method, Mack, Davis and Bartell [3] found that σ for gallium in an atmosphere of hydrogen and carbon dioxide at a temperature of 30.5-40° is 735 dynes/cm. Recently, Korol'kov [4] used the bubble pressure method to determine that the surface tension of gallium is 715 dynes/cm at a temperature exceeding the melting point by 50-80°.

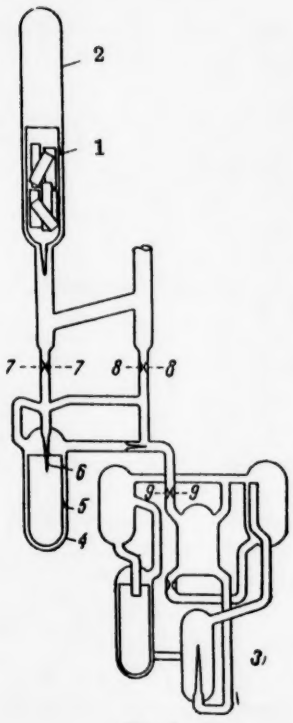

Fig. 1.

We have measured the surface tension of gallium in a vacuum over the temperature range of 30 to 500°, using for this purpose the maximum drop pressure method. The measurements were carried out in a gravitational apparatus which has been described in reference [5]. The system, which was constructed of glass, is shown schematically in Fig. 1. About 10 cc of solid metallic gallium was charged to funnel 1; tube 2, which contained funnel 1, was sealed, and a high vacuum was applied to the system. After a prolonged heat and vacuum treatment of gravitational apparatus 3 and reservoir 4, the gallium in funnel 1 was melted by means of a cylindrical electric furnace slipped over tube 2, and flowed through the narrow end of funnel 1 and tube 6, thereby being filtered free of oxides, into vessel 5, where it was then heated to a high temperature and maintained at this temperature for a period of several hours. This caused degasification of the metal, partial decomposition of organic compounds contained as impurities in the gallium, and distillation of some of the volatile impurities. Our experiments showed that degasification and purification of the gallium is especially good if the heating is carried out in a quartz apparatus at 1000°C.

After the metal had been heat treated, gravitational apparatus 3 and reservoir 4 were sealed off from the vacuum system along lines 7—7 and 8—8, and the molten gallium was then transferred to gravitational apparatus 3. The latter was then sealed, while hot, from reservoir 4 along line 9—9, and the measurements of the surface tension of the gallium were carried out in this apparatus in a manner similar to that used in the investigation of the surface tension of indium [5].

In order to calculate the surface tension, it was necessary to know the density of gallium; we did not carry out these measurements, but used instead the data of Spels [6]. The gallium used in the present investigation had a purity

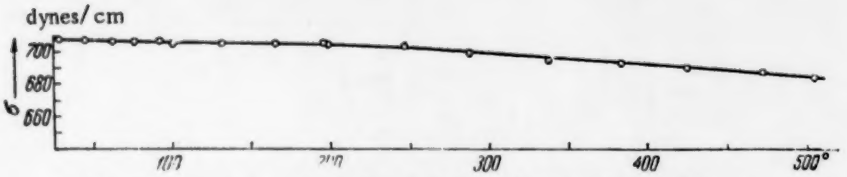

Fig. 2. Temperature dependence of the surface tension of gallium.

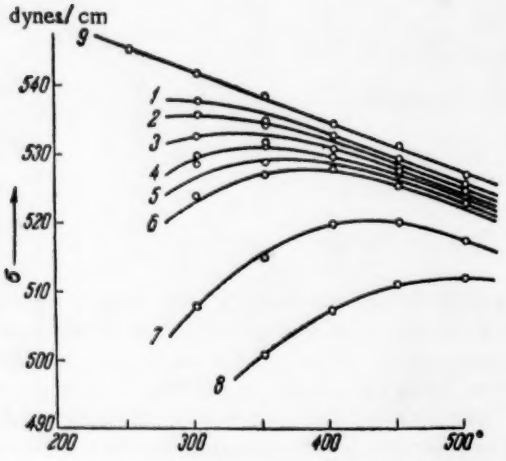

Fig. 3. Temperature dependence of the surface tension of tin and its alloys with tellurium according to the data of Pokrovskii and Kristian. Tellurium concentrations in atom percent: 1) 0.0037, 2) 0.0046, 3) 0.0104, 4) 0.0121, 5) 0.0140, 6) 0.0177, 7) 0.0364, 8) 0.0289, 9) pure tin.

TABLE 1

Temperature Dependence of the Surface Tension of Gallium.

Temp °C	Surface tension, dynes/cm		$\Delta\sigma=\sigma_{exp}-\sigma^{(1)}_{calc}$
	σ exp.	σ calc. (Eq. 1)	
30	707,0	706,6	+0,4
46	706,8	706,6	+0,2
63	706,1	706,5	—0,4
77	706,1	706,4	—0,3
93	706,3	706,2	+0,1
101	704,9	706,1	—1,2
132	704,9	705,5	—0,6
166	704,6	704,8	—0,2
196	705,2	703,8	+1,4
199	704,0	703,7	+0,3
247	703,0	701,9	+1,1
288	700,3	700,0	+0,3
338	695,9	697,3	—1,4
384	693,5	694,3	—0,8
424	690,9	691,4	—0,5
473	687,9	687,4	+0,5
505	684,7	684,5	+0,2

$\Delta\sigma_{av} = \pm 0,6$ dynes/cm

of 99.9%, but contained very small amounts of both surface-active and surface-inactive impurities. The results of our measurements of the surface tension of gallium are shown in Table 1 and graphed in Fig. 2. It may be seen that the surface tension is not a linear function of temperature, and the relationship may be represented by the equation

$$\sigma = 706.6 - 0.000647\,(t-29.79) - 0.0000965\,(t-29.78)^2, \qquad (1)$$

where t is the temperature in degrees C and 29.78 is the melting point of gallium according to Roeser and Hoffman [7].

As may be seen from Eq. 1, the temperature coefficient of the surface tension of gallium not only depends on temperature, but is astonishingly small as compared with $d\sigma/dT$ of other metals.

A nonlinear dependence of surface tension on temperature has been observed for many metals, for example, for cadmium [8, 9], mercury [8, 10-13], bismuth [14], copper [15], antimony [9,16], sodium [17], and selenium [18]. In cases where there is no reason to doubt the method or the experimental condition used in the measurements, the most probable reason for this phenomenon is the presence of surface-active impurities in the metal investigated. This was conclusively shown by Pokrovskii and Kristian, who found [19] that the addition of small amounts of tellurium to tin leads to a sharp change in the analytical dependence of surface tension on temperature and that there is a maximum on the polytherm of the surface tension of such alloys (Fig. 3). Metzger [20] recently established that the temperature coefficient of surface tension $d\sigma/dT$ for pure copper is negative; however, the addition of lead to the copper changed the sign of $d\sigma/dT$.

These measurements indicate that the study of the surface tension of ultrapure metals and of the effect of small amounts of impurities is of great theoretical interest and has important practical significance in new engineer-

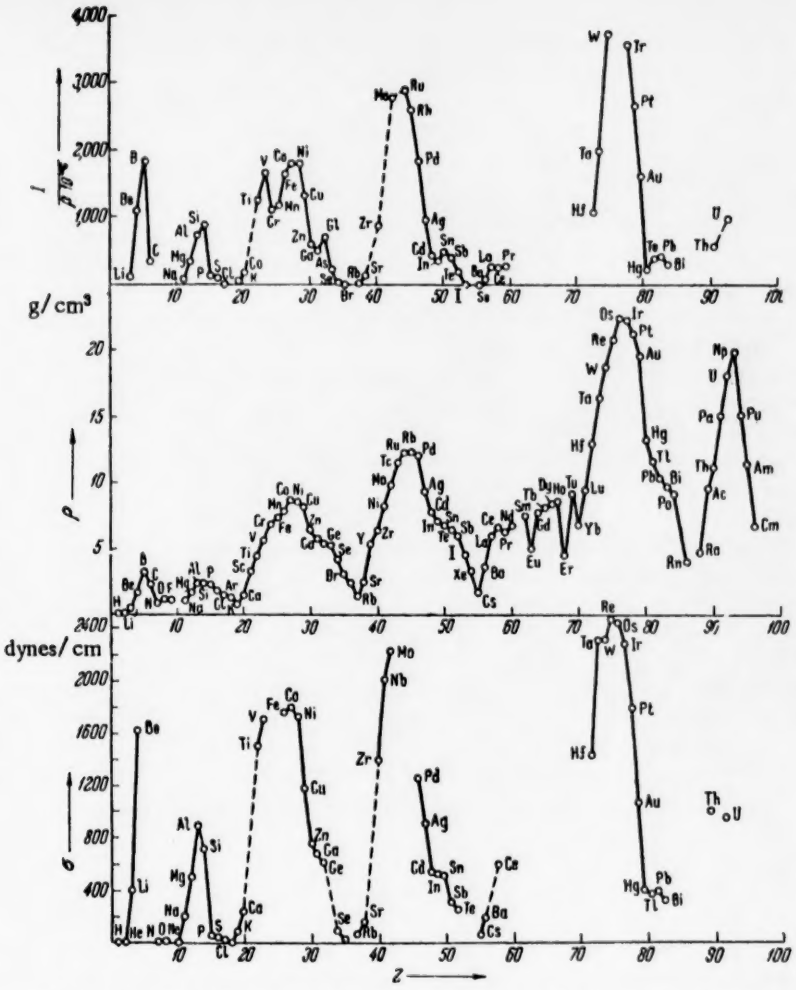

Fig. 4. Periodic dependence of certain properties of the elements on atomic number.

ing fields. The extent to which our data on the surface tension of gallium fit in with the periodic dependence of surface tension on the location of the element in the periodic system was also of interest to us. D. I. Mendeleev pointed out the periodic change in the density of elements with atomic number. This dependence was later found to apply to effective atomic and ionic radii, melting points of the elements, their ionization potentials, and other properties. In 1914, Smith [21] established a similar dependence for the surface tension of elements, which was later confirmed by work reported in references [22-25]. The dependence of the surface tension of elements on their position in the periodic system of D. I. Mendeleev is more clearly apparent at the present time (Fig. 4). Figure 4 shows not only experimental data, but also the most probable values of σ for certain metals calculated by Taylor [26] from various, chiefly thermodynamic, considerations. Figure 4 shows that surface tension of the elements, like other properties such as density and the reciprocal of the compressibility, is a periodic function of atomic number. As may be seen from Fig. 4, the regions of maxima and minima of these properties fall at the same groups of elements. It would be expected from a comparison of these relationships that the surface tension of gallium would be higher than that of germanium but lower than the surface tension of zinc, as was confirmed by our experiments. Somewhat earlier, during a study of the surface tension of indium [5], on the basis of the periodic dependence of σ of the elements on atomic number we expected that σ for indium would be approximately the same as the surface tension of cadmium and tin, and this has been experimentally confirmed [5, 27].

These examples are not the only ones; the general regularities existing between surface tension and other

properties of the elements, on the one hand, and their atomic number, on the other, indicate a deep-seated connection between surface and bulk properties of substances.

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INVESTIGATION OF THE REGULARITIES FOUND IN THE ALKYLATION OF XYLENES WITH PROPYLENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$

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The alkylation of o-, m-, and p-xylenes with propylene in the presence of $BF_3 \cdot H_3PO_4$ is a simple and convenient method for the synthesis of mono- and diisopropylxylenes, and by oxidation of these compounds it is possible to prepare derivatives of benzoic acid and phthalide, benzenepolycarboxylic acids, phenols, ketones, and other interesting substances [1]. Moreover, the study of this process provides material suitable for establishing regularities in the formation of polyalkylbenzenes. The propylation of m- and p-xylenes in the presence of $BF_3 \cdot P_2O_5$ and of m-xylene in the presence of $BF_3 \cdot H_3PO_4$ has been studied by Kirkland et al. [2]; however, these authors gave no consideration to the rules governing these reactions, and were unable to obtain yields of isopropylxylenes in excess of 52%.

TABLE 1

Hydrocarbon	B.p., °C	M.p., °C	n_D^{20}	d_4^{20}
o-Xylene	144,5	—	1,5055	0,8806
m-Xylene	139,0	—	1,4971	0,8642
p-Xylene	138,4	13,2	1,4958	0,8611
4-Isopropyl-o-xylene	199,5	—	1,5096	0,8713
3-Isopropyl-o-xylene	204,5	—	1,5102	0,8940
4-Isopropyl-m-xylene	197,8	—	1,5013	0,8770
5-Isopropyl-m-xylene	194,6	—	1,4950	0,8606
2-Isopropyl-p-xylene	196,0	—	1,5010	0,8762
4,5-Diisopropyl-o-xylene	239,5	—	1,5015	0,8809
4,6-Diisopropyl-m-xylene	236,0	16,5	1,4980	0,8720
2,5-Diisopropyl-p-xylene	244,0	37,4	—	—

The present work was devoted to a systematic investigation of the effect of catalyst concentration, temperature, reaction time, and mole ratio of reactants on the yield and composition of reaction products from the alkylation of o-xylene (I), m-xylene (II), and p-xylene (III). Conditions were found which made it possible to prepare isopropylxylenes in yields of about 90% of theoretical which established the relative reactivities of xylenes and isopropylxylenes, and which clarified the kinetic features of the reactions. Alkylation and distillation of the catalyzates were carried out by previously described methods [3].

Determination of the alkylate compositions showed that propylation of (I) formed 4-isopropyl-o-xylene (IV), 3-isopropyl-o-xylene (V), and 4,5-diisopropyl-o-xylene (VI); (II) gave 4-isopropyl-m-xylene (VII), 5-isopropyl-m-xylene (VIII), 2-isopropyl-m-xylene (IX), 4,6-diisopropyl-m-xylene (X), and 2,5-diisopropyl-m-xylene (XI). The monoalkylation product of (III) consisted exclusively of 2-isopropyl-p-xylene (XII), and 2,5-diisopropyl-p-xylene (XIII) was the predominant compound in the dialkylation products. The isomers were separated by rectification in a column of 45-50 theoretical plates; (X) and (XIII) were purified by freezing and recrystallization. The principal constants of the compounds obtained and the characteristics of the original xylenes are shown in Table 1 and are in agreement with the data of references [2,4]. Hydrocarbons (V) and (VI) have not been described in the literature.

The compositions of the mixtures of isomers were determined by oxidation to benzenepolycarboxylic acids, by refractometry, and by means of the infrared absorption spectra. The first method was primarily used for identification of the reaction products and for semiquantitative determination of the percentage compositions of mixtures of isomers, and the second method was primarily used for rapid determination of the relative amounts of (IV) and (V) and of (VII) and (VIII) (the difference in refractive indices allowed us to establish concentrations with an accuracy of 2-5%).

Separation of the benzenetricarboxylic acids was based on the fact that trimellitic acid, unlike hemimellitic and trimesic acids, methylates to the liquid trimethyl ester which is readily separated from the high-melting trimethyl esters and from the soluble 1,3-dimethyl ester of hemimellitic acid. The esters were identified by melting point, and were converted by hydrolysis to the corresponding acids. The trimellitic acid (product of the oxidation of (IV), (VII), and (IX)) had a m. p. of 228-234° (with decomposition), the hemimellitic acid melted at 193-196° (with decomposition) and its dimethyl ester at 149°, and the trimethyl and triethyl esters of trimesic acid melted at 144 and 135.5°, respectively, which agrees with the data of reference [5]. Mixtures of the above substances with known, pure preparations melted without depression of the melting point.

The isopropylxylenes were oxidized to benzenetricarboxylic acids with nitric acid in an autoclave at 200° and a reaction time of 8-10 hours. In order to obtain tribasic acids as the major product (80-95% yield), it was necessary to use 45 weight parts of 20-25% HNO_3 for 1 weight part of hydrocarbon. It was possible to obtain incomplete oxidation of the hydrocarbons under milder conditions. For example, refluxing of (IV) with excess 10% HNO_3 (atmospheric pressure) converted it to 3,4-dimethylbenzoic acid (m. p. 166°) in 45-53% yield, while 25% HNO_3 converted it to a mixture of methylbenzenedicarboxylic acids. Isopropylxylenes (V), (VII), and (IX) were oxidized with 10-15% HNO_3 in an autoclave at 180°and a reaction time of 3 hours to trimellitic acid (30-40%) and dimethylphthalidecarboxylic acid (56-60%). The latter were also prepared by alkaline $KMnO_4$ oxidation of the hydrocarbons (yield 25%) and have been similarly obtained from trimethylphthalides [1]. By a combination of the action of nitric acid and an alkaline solution of $KMnO_4$ we were able to oxidize (VI), (X), and (XIII) to pyromellitic acid (m. p. 276-280°, m. p. of the tetramethyl ester 142°); however, the yield was only 20-23%, since the reaction was stopped at the formation of a mixture of incompletely oxidized products, or (under vigorous conditions) the substance decomposed.

Oxidation of (XIII) in an autoclave gave the dilactone of 2,5-di(α-hydroxyisopropyl)terephthalic acid, which distilled without decomposition at 325° (8% yield). We were unable to obtain benzene-1,2,3,5-tetracarboxylic acid, although spectroscopic analysis showed that 1,2,3,5-tetraalkylbenzene was present in the mixture of diisopropyl-m-xylenes, along with (X) which was present to the extent of 80-90% of the fraction. The isopropylxylenes were also identified by means of oxidation. Thus, (IV) was oxidized with atmospheric oxygen in the presence of 3 mg/mole of manganese resinate at 110° and a reaction time of 4 hours to a hydroperoxide content of 21%. Decomposition of the hydroperoxides with concentrated H_2SO_4 gave a 64% yield of 3,4-dimethylphenol with an m. p. of 62.5°, 3,4-dimethylphenoxyacetic acid with an m. p. of 162°, and acetone (m. p. of the 2,4-dinitrophenylhydrazone 125°). The other oxidations products have been described by us previously [1].

The results of certain experiments on the propylation of xylenes are summarized in Table 2. In addition to the composition of the reaction mixtures and the product yields, Table 2 also lists for easy reference the apparent ratios of the rate constant for the alkylation of the isopropylxylenes and the original xylene ($r = k_2/k_1$); the actual extent of alkylation is also shown. The values of $\underline{r}$ and $\underline{q}$ were determined by the formula

$$q = M + 2D,\ M = (U^r - U)/(1 - r). \qquad (1)$$

where U, M, and D are, respectively, the mole fractions of xylene and mono- and diisopropylxylenes in the catalyzate [6].

The data of Table 2 show that an increase in temperature and concentration of $BF_3 \cdot H_3PO_4$ caused a decrease in the relative rate of formation of secondary alkylation products. This feature, which was first discovered by one of us together with Kurashev and Paushkin in the alkylation of benzene with propylene [7], is probably characteristic of all alkylations of aromatic hydrocarbons with olefins in the presence of $BF_3 \cdot H_3PO_4$. It is easy to show with the aid of the equation $\log(r_{T_1}/r_{T_2})/\log(r_{T_1}/r_{T_3}) = T_3(T_2 - T_1)/T_2(T_3 - T_1)$, which is readily derived from the Arrhenius equation (r_{T_1} – is the ratio k_2/k_1 at an absolute temperature T_1), that the effect of temperature on the value of $\underline{r}$ is more complex than would be expected. For example, for $r_{293} = 0.6$ and $r_{323} = 0.27$, r_{353} should be 0.15; in actuality, this prediction fails, and the values of $\underline{r}$ at 50 and 80° are practically equal.

TABLE 2*

Expt. No.	Amt. reactants (centimol. per mol. xylene) $BF_3 \cdot H_3PO_4$	propylene	q·100	Temp., °C	Propylene feed rate, centimoles/hour	Composition of reaction mixture and yields of alkylation products: xylene mole %	isopropylxylenes mole %	isopropylxylenes % of theoretical	diisopropylxylenes mole %	diisopropylxylenes % of theoretical	r	Isopropylxylene composition, %: 1, 2, 4	1, 2, 3	1, 3, 5
1	2,5	50	42,0	60	10	61,6	34,8	69,6	3,6	14,4	0,38	75	25	—
2	5,0	52	50,8	60	15	53,1	43,0	82,7	3,9	15,0	0,25	80	20	—
3	7,5	51	50,4	60	20	52,7	44,2	86,5	3,1	12,3	0,19	—	—	—
4	10	50	49,7	60	25	52,9	44,5	89,0	2,6	10,4	0,17	85	15	—
5	20	50	49,6	60	25	52,8	44,8	89,6	2,4	9,6	0,16	88	12	—
6	10	60	49,4	20	15	57,4	35,8	59,7	6,8	22,6	0,59	60	40	—
7	10	51	50,5	40	20	53,0	43,5	85,3	3,5	13,7	0,22	—	—	—
8	10	51	50,8	50	25	52,2	44,8	87,9	3,0	11,8	0,18	—	—	—
9	10	50	49,7	80	25	52,7	44,9	84,8	2,4	9,6	0,15	96	4	—
10	10	60	56,8	60	40	48,2	46,8	78,0	5,0	16,6	0,25	80	20	—
11	10	60	50,9	60	60	55,3	38,5	64,2	6,2	20,7	0,41	65	35	—
12	10	80	79,0	60	10	30,2	60,6	75,7	9,2	23,0	0,20	76	24	—
13	10	33	33,0	60	20	68,1	30,8	93,3	1,1	6,6	0,17	—	—	—
14	10	31	30,4	60	20	70,9	27,8	89,9	1,3	8,4	0,26	68	2	30
15	10	78	76,5	60	25	33,4	56,7	72,7	9,9	25,4	0,25	65	2	33
16	10	65	61,0	20	15	50,0	39,0	60,0	11	33,8	0,62	70	2	28
17	10	30	27,4	50	15	73,6	25,4	84,6	1,0	6,7	0,27	100	—	—
18	10	50	39,9	20	10	65,1	29,9	59,8	5,0	20,0	0,60	100	—	—
19	10	30	29,2	80	15	72,0	26,8	89,3	1,2	8,0	0,25	100	—	—
20	10	40	39,6	60	10	62,9	34,6	86,5	2,5	12,5	0,26	100	—	—

* Propylation of o-xylene was studied in Experiments 1-13, m-xylene in Experiments 14-16, and p-xylene in Experiments 17-20.

Temperature and, particularly, catalyst concentration had no great effect on the true ratio of alkylation rate constants for xylene and isopropylxylene [3]. It is impossible to explain this by dealkylation of diisopropylbenzenes, since the rate of this process is too low (at 60-80° K = 0.005−0.008 hours^{-1}).

There is basis to suppose that in this case the matter is simple. When reaction conditions do not provide a high rate of addition of olefin to the aromatic hydrocarbon, the concentration of alkylating agent in the reaction zone will increase, tending toward some maximum value, and this will promote both polymerization of the olefin and formation of products of the alkylation of aromatic hydrocarbons by the polymers on the one hand, and secondary alkylation, on the other (see the experiments at high propylene feed rates). And indeed, when the temperature was low and the catalyst concentration was insufficient, numerous polyalkylbenzenes were always formed and there was considerable polymerization of the olefin. With an improvement in reaction conditions, the values of r rapidly approached the true rate constant ratio for alkylation of isopropylxylenes and xylene, becoming, finally, practically constant. The data of Table 2 and Fig. 1 persuasively show that alkylation of xylenes proceeds as a quasihalogen, irreversible stepwise reaction under suitable conditions.

In our study of the effect of various factors on the ratio of isomers it was noted that (IV) and (VIII) are formed not only directly by an attack on the corresponding position of the xylene nucleus, but also as a consequence of the isomerization of (V) and (VII). Numerous investigators from the time of Jacobsen and Anschütz [8] down to the present [9] have explained the isomerization reactions (including the abnormal fomation of 1,3 and 1,3,5 forms) by dealkylation of polyalkylbenzenes. However, our experimental data cannot be explained by this theory, since with $BF_3 \cdot H_3PO_4$ the rate of isomerization is ten times greater than the rate of dealkylation. For example, (V) is so rapidly converted to (IV) at 80° that after only 4-5 hours it was impossible to establish the presence of the original hydrocarbon in the isomerizate even by spectroscopic analysis. (VII) isomerized to (VIII) to an extent of approximately 98% in 20 hours at 60-80°. In both cases, products of the disproportionation of the isopropylxylenes were formed in amounts not exceeding 1%. 1,2,4-Triisopropylbenzene and the 1,2,3,5-dimethyldiisopropylbenzenes, except (XI), underwent isomerization readily. The dialkylbenzenes were converted to the m-isomers very slowly, and hydrocarbons (IV), (VI), and (VIII)-(XIII) were generally unchanged by the action of

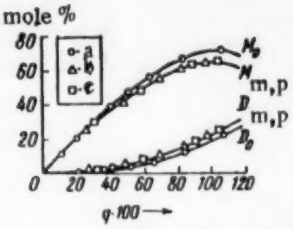

Fig. 1. Alkylation of xylenes with propylene at 60° in the presence of 0.1 mole/mole of $BF_3 \cdot H_3PO_4$. The curves were calculated by Eq. (1), $k_2/k_1 = 0.17$ for alkylation of o-xylene and 0.25 for alkylation of m- and p-xylenes. a, b, and c are, respectively, the experimental amounts of alkylation products from o-xylene (M_0, D_0) and m- and p-xylenes ($M_{m,p}$ $D_{m,p}$).

$BF_3 \cdot H_3PO_4$. On the basis of these facts, the regularities in the isomerization of polyalkylbenzenes can be formulated as follows: migration of an isopropyl group is intramolecular in nature, and is accomplished mainly when alkyl radicals are present in 2,3-, 2,4-, and 2,3,5-positions relative to the isopropyl group.

There was practically no isomerization of the hydrocarbons at 20-25°, and migration of a methyl radical did not take place even at 100°. All of these regularities not only explain the nature of substituent orientation, for example, the reason for the formation of a mixture of (XI) and (X) etc. during propylation of (VIII), but they also point out methods for controlling the process to obtain the desired materials in maximum yield.

Alkylation of xylenes with propylene in the presence of $BF_3 \cdot H_3PO_4$ can be recommended for the synthesis of (IV), (VI), (VIII), (XII), (XIII), and, possibly even (V), since separation of (IV) and (V) is easily accomplished with a good column.

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SPECTROPHOTOMETRIC DETERMINATION OF THE MOLECULAR WEIGHTS OF SOME INNER-COMPLEX COMPOUNDS

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Experimentally determined molecular weights are very important for characterization purposes in studies of inner-complex compounds. However, cryoscopic and ebullioscopic methods cannot always be used owing to the low solubility of inner-complex compounds in the usual solvents.

In this case, the recently proposed method for the determination of molecular weights by absorption spectra is most convenient. This method was first used for the determination of the molecular weights of picrates [1], and it has since been applied to the determination of the molecular weights of other organic and complex compounds [2,3]. The basis of this method lies in the assumption that for compounds containing the same chromophore group the molar absorption coefficient, E, of the chromophore group is constant for all such substances, while the optical density, d, depends on the molecular weight of the absorbing substance.

Hence, if K_{sp} and K^{x}_{sp} are the specific absorption coefficients, then $K'_{sp} = \frac{d'}{C'_w l}$ and $K^{x}_{sp} = \frac{d^{x}}{C^{x}_w l}$, where C_w and C^{x}_w are weight concentration in grams per liter, d' and d^{x} are the optical densities of the solutions, and l is the thickness of the absorbing layer. On the other hand, $K'_{sp} = \frac{\epsilon'}{M'}$ and $K^{x}_{sp} = \frac{\epsilon^{x}}{M^{x}}$, and since $\epsilon' = \epsilon^{x}$,

$$M^{x} = M' \frac{K'_{sp}}{K^{x}_{sp}}$$

Consequently, knowing the concentrations by weight and the optical densities of the absorbing solutions it is possible to calculate the specific absorption coefficients, K_{sp}, and knowing the molecular weight of one of the substances it is possible to determine the molecular weight of the compound under investigation.

The present article considers the possibility of using a spectrophotometric method for the determination of molecular weights of inner-complex compounds of the Mannich base type formed by derivatives of 8-hydroxyquinoline with a number of divalent cations. Extension of this method of molecular weight determination to inner-complex compounds appeared feasible inasmuch as the absorption spectra of the inner-complex compounds investigated are identical to the absorption spectra of the chelate forming substances (Mannich bases) in the wavelength region of 290-350 mμ. The compound of known molecular weight was, in each case, the 8-hydroxyquinoline derivative with which the complex was formed. Absorption spectra were obtained for solutions in redistilled dioxane. An SF-4 spectrophotometer was employed, and all spectra were taken at room temperature. Since absorption spectra of Mannich bases are affected by the nature of the substituents, the optical densities of each Mannich base and the complexes formed from it were measured at an appropriately selected wavelength. Since the composition of an inner-complex compound may be expressed by the general formula $Me(OM)_2$, where HOM is the Mannich base molecule, only equivalent weights were determined. The formula used for calculating molecular weight has the form:

$$M^{C} = 2\left[(M^{b} - 1) \frac{K^{b}_{sp}}{K^{C}_{sp}} \right]^{*}.$$

*b = base; C = complex.

TABLE 1

Molecular Weights of Complexes

Name of complex	Formula	Wave-length mμ	K_{sp} of base	K_{sp} of complex	Equiv. wt.	Mol. wt.	Mol. wt. calc.	Error, %
Tungsten 7-(m-nitro-anilinobenzyl)-8-hydroxyquinolate	$(C_{22}H_{16}N_3O_3)_2WO_2$	324	100,00	75,00	494,0	988	957	—3,12
Molybdenum 7-(m-nitroanilinobenzyl)-8-hydroxyquinolate	$(C_{22}H_{16}N_3O_3)_2MoO_2$	324	100,00	87,5	424	848	869	+2,41
Copper 7-(m-nitro-anilinobenzyl)-8-hydroxyquinolate	$(C_{22}H_{16}N_3O_3)_2Cu$	324	100,00	90,62	409	818	804	—1,74
Nickel 7-(m-nitro-anilinobenzyl)-8-hydroxyquinolate	$(C_{22}H_{16}N_3O_3)_2Ni$	324	100,00	96,87	396	792	799	+0,87
Tungsten 7-(m-nitro-anilinofurfuryl)-8-hydroxyquinolate	$(C_{20}H_{14}N_3O_4)_2WO_2$	300	262,5	197,5	480	960	937	—2,44
Molybdenum 7-(m-nitroanilinofurfuryl)-8-hydroxyquinolate	$(C_{20}H_{14}N_3O_4)_2MoO_2$	300	262,5	216,63	439	878	848	—3,53
Nickel 7-(o-nitro-anilinofurfuryl)-8-hydroxyquinolate	$(C_{20}H_{14}N_3O_4)_2Ni$	324	120,6	109,4	398	796	778	—2,31
Tungsten 7-(p-nitro-anilinopiperonyl)-8-hydroxyquinolate	$(C_{23}H_{16}N_3O_5)_2WO_2$	298	300,0	237,5	524,7	1049	1043	—0,57

The results are presented in Table 1.

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POLAROGRAPHIC STUDY OF NITRO-ACI TAUTOMERISM OF NITROCYCLOHEXANE

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The polarographic method previously developed by the present authors [1] for the analysis of nitrocyclohexane (NCH) has made it possible to study the kinetics and equilibrium of the nitro-aci tautomeric conversion of NCH. In contrast to similar polarographic investigations of other compounds [2, 3], we studied not only the nitro-aci conversion and the reverse reaction, but also the corresponding equilibrium*. The nitro-form of NCH gives a clear wave over a broad pH interval; the aci-form is not reduced at a dropping mercury electrode.

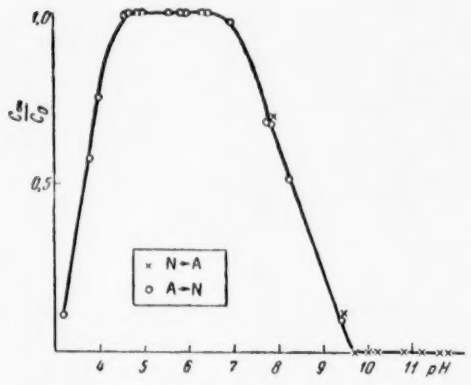

Fig. 1.

The initial NCH solutions (~ 0.01 M) were prepared in water or in an alkaline solution depending on the direction in which the reaction was to be studied. Citrate-phosphate and alkaline tetraborate buffer mixtures with added KCl served as supporting electrolytes to maintain constant ionic strength, $\mu = 1.0-1.4$. The concentration of the nitro-form of NCH was recorded as a function of time by means of a PÉ-312 electronic polarograph. The study of the nitro-aci conversion (N → A) was carried out over a pH interval of 8-12, and the reverse reaction was studied in the pH range of 3-9.5. The investigation was carried out at temperatures of 25, 32, 40, and 50° C.

Figure 1 shows the dependence of the ratio C_∞/C_0 on pH at 25° C; C_0 – is the initial concentration of NCH in the nitro- or aci-form, and C_∞ – is the concentration of the nitro-form of NCH at completion of the reaction.

As may be seen from Fig. 1, the nitro-form of NCH was completely converted to the aci-form at a pH > 9.5, and the aci-form was completely converted to the nitro-form at a pH of 4.5-7.0. Equilibrium was obtained at a pH of 7.0-9.5, and this equilibrium could be approached from either side. The decrease in C_∞/C_0 at a pH less than 4.5 (A → N) can apparently be explained by the simultaneous conversion of the aci-form to cyclohexane by the Nef reaction [5] at this low pH.

The kinetic data obtained are well described by the following equations (Figs. 2, 3, and 4; $\underline{h}$ is the wave height):

* The possibility of a polarographic study of aci-nitro conversion of nitromethane was mentioned in reference [4].

$$K_0 a_{OH^-} = K_N = \frac{2{,}3}{t} \lg \frac{C_0}{C_N} \quad (N \rightarrow A); \tag{1}$$

$$\frac{K'_0 a_{H^+}}{1 + \frac{a_{H^+}}{K_1} + \frac{a^2_{H^+}}{K_1 K_2}} = K_A = \frac{2{,}3}{t} \cdot \frac{C_\infty}{C_0} \lg \frac{C_\infty}{C_\infty - C_N} \quad (A \rightarrow N), \tag{2}$$

where C_N is the concentration of the nitro-form at time t, K_N is the experimental reaction rate constant for $N \rightarrow A$ at constant pH, K_A is the rate constant for the reaction $A \rightarrow N$; K_0, K'_0, K_1, K_2 are constants for a given ionic strength, and a_{H^+} and a_{OH^-} are the activities of the hydrogen and hydroxyl ions.

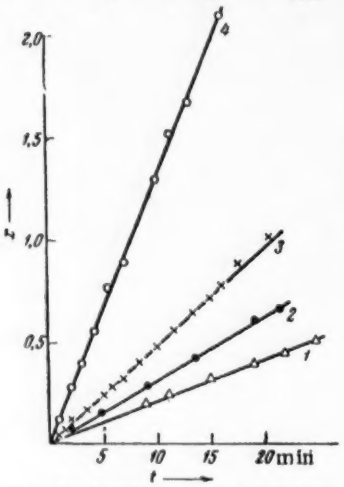

Fig. 2. 1) pH 10.8, h_0 = 7.6 cm, h_∞ = 0; 2) pH 4.0, h_0 = 7.5 cm. h_∞ = 5.7; 3) pH 5.0, h_0 = h_∞ = = 7.8; 4) pH 11.6, h_0 = 7.6 cm, h_∞ = 0. For 1, 4 $N \rightarrow A$, $x = \log \frac{h_0}{h_t}$; for 2, 3, $A \rightarrow N$, $x = \frac{h_\infty}{h_0} \lg \frac{h_\infty}{h_\infty - h_t}$.

At constant pH, Eq. (1) corresponds to a first order reaction, and in this region it is in agreement with the data of references [2, 3] on nitro-aci conversion of other substances.

At constant pH and in the region of complete conversion of A to N (pH of 4.5-7.0), Eq. (2) also corresponds to a first order reaction, while at less than 100% yield of the nitro-form (pH < 4.5) – it corresponds to two parallel first order reactions. Values of K_N and K_A at 25° and various pH are shown in Table 1. The relationship between log K_N and pH is linear (Fig. 3), while the graph of log K_A against pH passes through a maximum at pH ≅ 5 (Fig. 4).

On the basis of the concepts of acid-base catalysis of the nitro-aci tautomeric conversion [6], we may present the following mechanism for the reactions studied:

$$\xleftarrow[K''_0]{\text{Nef reaction}} [C_6H_{10} : NO_2H]\,H^+ \underset{K_2}{\overset{H^+}{\rightleftarrows}} C_6H_{10} : NO_2H \underset{K_1}{\overset{H^+}{\rightleftarrows}}$$

$$\underset{K_1}{\overset{H^+}{\rightleftarrows}} C_6H_{10} : NO_2^- \underset{\text{OH},\ K_0}{\overset{\text{slow step}\ H^+,\ K_0}{\rightleftarrows}} C_6H_{11}NO_2, \tag{3}$$

slow step

where K_0, K'_0, K''_0 – rate constants, respectively,

$$K_1 = \frac{[C_6H_{10} : NO_2^-]\,[H^+]}{[C_6H_{10} : NO_2H]},$$

and K_2 is the same for the protonated complex: $[C_6H_{10} : NO_2H]H^+$.

This mechanism yields kinetic equations agreeing with Experiments (1) and (2) with the following values of the constants (25°): K_0 = 50 (mole/liter)$^{-1}$ · min^{-1}, $K'_0 = 2.8 \cdot 10^5$ (mole/liter)$^{-1}$ · min^{-1}, K''_0 = 0.11 min^{-1}, $K_1 = 4.3 \cdot 10^{-7}$ and $K_2 = 2.3 \cdot 10^{-4}$.

In Fig. 4, the points represent experimental data, and the curves are calculated. The corresponding activities were used in place of C_{H^+} and C_{OH^-} in the calculations.

It follows from this mechanism that a protonated complex $[C_6H_{10} : NO_2H]H^+$ takes part in the limiting step of the Nef reaction (at a pH of less than 4.5). A similar proposal has been made relative to the participation of acids in analogous reactions [7].

Since isomerization of NCH is catalyzed by hydroxyl ions at a pH ≥ 9.7 and by hydrogen ions at a pH≤7, the equilibrium constant cannot be calculated from the ratio K_0/K'_0. The experimentally determined equilibrium constants (for the equilibrium $N \rightleftharpoons A$ in the pH region 7.0-9.5) are shown in Table 2 (25°). The equilibrium constants were calculated by the equation:

$$K_e = \frac{[C_6H_{10} : NO_2^-]\,a_{H^+}}{[C_6H_{11} : NO_2]}.$$

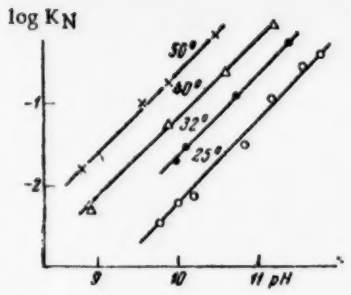

Fig. 3.

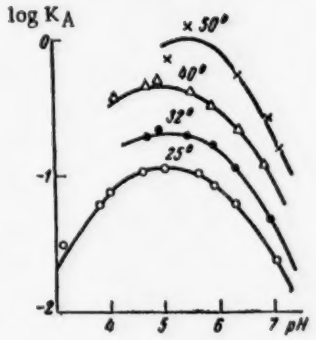

Fig. 4.

TABLE 1

pH	K_N, min^{-1}	pH	K_A, min^{-1}
		3,1	$3,0\cdot10^{-2}$
9,7	$3,4\cdot10^{-3}$	3,8	$5,6\cdot10^{-2}$
10,0	$6,4\cdot10^{-3}$	4,0	$7,5\cdot10^{-2}$
10,2	$7,8\cdot10^{-3}$	4,6	0,10
10,8	$4,8\cdot10^{-2}$	5,0	0,11
11,2	0,12	5,2	$9,5\cdot10^{-2}$
11,6	0,29	5,6	$9,8\cdot10^{-2}$
11,8	0,38	5,9	$8,1\cdot10^{-2}$
		6,3	$6,1\cdot10^{-2}$
		7,0	$2,3\cdot10^{-2}$

TABLE 2

pH	Initial form of NCH	$\frac{C_{\infty}}{C_0}$	$K_e \cdot 10^9$
7,9	aci	0,67	6,1
7,9	aci	0,65	6,8
7,9	nitro	0,70	5,3
7,9	nitro	0,65	6,8
8,2	aci	0,51	6,0
9,4	aci	0,10	3,5
9,4	nitro	0,11	3,1
			5,0± 1,0

$[C_6H_{10}:NO_2^-]$ was determined by means of the values of K_1 and K_2.

As Table 2 shows, values of K_e obtained during approach to equilibrium from either direction are in good agreement. Activation energies for the processes were determined from linear graphs of log K_0 – 1/T and log K_0' – –1/T: N → A, 18.4 kcal/mole and A → N, 16.0 kcal/mole.

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COMPLEXES FORMED BY AROMATIC ORGANOZINC COMPOUNDS OF THE CLASS ArZnX

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As has been shown by a number of investigators and was more recently noted by Blaise [1], organozinc compounds cannot be prepared by direct reaction of halogen derivatives of aromatic compounds with metallic zinc in the presence of any of the presently available catalysts. For the synthesis of solutions of organozinc compounds Blaise proposed a reaction between zinc halides in ether and organomagnesium compounds obtained by the usual Grignard route.

While this method may be useful for preparing the original organozinc compounds to be used in subsequent syntheses (for example, the preparation of ketones) [2], it can hardly shed any light on the question of mixed organozinc compounds.

The complexity of the composition of the Grignard reagent itself and, moreover, the presence in the latter of magnesium salts and their etherates complicate the picture even more. It is not suprising, therefore, that in an experiment in which he reacted zinc chloride with phenylmagnesium bromide and separated a crystalline compound from the solution, Blaise [1] obtained a complicated magnesium–zinc complex of the composition*:

$$(C_2H_5)_2O \cdot MgCl_2 \cdot (C_2H_5)_2O \cdot C_6H_5ZnBr$$

or

$$(C_2H_5)_2O \cdot MgClX \cdot (C_2H_5)_2O \cdot C_6H_5ZnCl.$$

However, as we were the first to show [3], mixed organozinc compounds can be prepared by disproportionation of their complexes with ether or dioxane. A method developed by the present authors [4] for the preparation of diaryl compounds of zinc through crystalline organolithium compounds permits a rather extensive investigation of the aromatic series.

The complexes–white crystalline substances which were obtained in good yields–did not have definite melting points. They reacted vigorously with water or alcohol, and they readily reacted with acyl halides to form ketones.

The zinc analyses were carried out by combusting the compound together with nitric acid in a quartz tube and subsequently calcining to zinc oxide.

Experimental

All syntheses and separations were carried out in an atmosphere of inert gas (nitrogen or argon) and in dry solvents.

* The formulas are as given by the author.

The initial diarylzinc compounds were prepared through the crystalline organolithium compounds by a method previously developed by us [4].

Preparation of crystalline etherates of the general formula $ArZnX(C_2H_5)_2O$.* A solution of the diarylzinc in the minimum amount of absolute ether required for solution was mixed with a solution of the appropriate zinc halide in the same amount of ether (mole ratio of zinc halide to diarylzinc of 0.96-0.98), and two-thirds of the ether was then distilled. The resulting white crystalline precipitate was suction filtered, washed with cold ether, and dried under vacuum. The corresponding mixed organozinc compound was obtained in sufficient purity so that a second crystallization was not required prior to analysis.

TABLE 1

Etherate	Yield, %	Analysis			
		Found		Calculated	
		Zn	halogen	Zn	halogen
$C_6H_5ZnBr\cdot(C_2H_5)_2O$	70,5	21,96 21,77	26,97 27,35	22,08	26,96
$C_6H_5ZnI\cdot(C_2H_5)_2O$	79,0	18,63 19,16	36,67 37,03	19,05	36,97
$o\text{-}CH_3C_6H_4ZnCl\cdot(C_2H_5)_2O$	55,1	25,08 24,66	13,27 13,00	24,60	13,35
$o\text{-}CH_3C_6H_4ZnBr\cdot(C_2H_5)_2O$	66,7	21,40 21,40	26,25 25,60	21,08	25,74
$o\text{-}CH_3C_6H_4ZnI\cdot(C_2H_5)_2O$	82,6	18,51 18,12	35,33 35,55	18,30	35,52
$p\text{-}CH_3C_6H_4ZnCl\cdot(C_2H_5)_2O$	52,0	25,01 24,81	13,70 13,34	24,60	13,35
$p\text{-}CH_3C_6H_4ZnBr\cdot(C_2H_5)_2O$	72,5	21,10 21,44	25,76 26,05	21,08	25,74
$p\text{-}CH_3C_6H_4ZnI\cdot(C_2H_5)_2O$	70,0	18,66 18,41	35,13 35,07	18,30	35,52
$\alpha\text{-}C_{10}H_7ZnCl\cdot{}^1/_2(C_2H_5)_2O$	65,3	25,09 24,91	13,40 13,46	24,69	13,40
$\alpha\text{-}C_{10}H_7ZnBr\cdot{}^1/_2(C_2H_5)_2O$	95,0	20,82 20,71	25,44 25,26	21,14	25,83
$\alpha\text{-}C_{10}H_7ZnI\cdot(C_2H_5)_2O$	61,9	16,80 16,45	31,70 31,93	16,63	32,27

All of the etherates were white crystalline substances, readily soluble in ether, dioxane, ethyl acetate, and pyridine and insoluble in benzene, hexane, carbon tetrachloride, and chloroform (Table 1).

Synthesis of crystalline dioxanates of the general formula $ArZnX\cdot C_4H_8O_2$. A solution of the diarylzinc in the minimum amount of absolute ether was mixed with a solution of the zinc halide (at a mole ratio of diarylzinc to zinc halide of 0.97-0.98) in the same amount of absolute ether. The solution was allowed to stand for several hours, and dry 1,4-dioxane (in three-fold excess over that required for precipitation of the dioxanate) was then added. The larger part of the solvent was distilled under vacuum, and the resulting white crystalline precipitate was suction filtered, washed with cold petroleum ether, and dried under vacuum.

All of the dioxanates were white crystalline substances, soluble in pyridine, dioxane, absolute ether, and ethyl acetate and insoluble in benzene, hexane, and carbon tetrachloride (Table 2).

*Or $Ar_2Zn\cdot ZnX_2\cdot 2(C_2H_5)_2O$.

TABLE 2

Dioxanate	Yield, %	Analysis			
		Found		Calculated	
		Zn	Halogen	Zn	Halogen
$C_6H_5ZnI \cdot C_4H_8O_2$	58,0	17,80 17,90	35,10 36,02	17,81	35,60
$o\text{-}CH_3C_6H_4ZnCl \cdot C_4H_8O_2$	77,6	23,91 23,16	13,10 13,20	23,36	12,68
$o\text{-}CH_3C_6H_4ZnBr \cdot C_4H_8O_2$	83,3	20,53 20,05	24,57 24,31	20,16	24,65
$o\text{-}CH_3C_6H_4ZnI \cdot C_4H_8O_2$	86,0	18,05 17,48	34,80 34,01	17,62	34,18
$p\text{-}CH_3C_6H_4ZnCl \cdot {}^1/_2C_4H_8O_2$	71,0	28,13 27,88	14,62 14,55	27,71	15,04
$p\text{-}CH_3C_6H_4ZnBr \cdot {}^1/_2C_4H_8O_2$	75,0	23,08 23,64	28,03 28,16	23,32	28,50
$p\text{-}CH_3C_6H_4ZnI \cdot C_4H_8O_2$	72,0	17,20 17,23	34,60 34,01	27,62	34,18

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THERMODYNAMICS OF THE ABSORPTION OF PROPYLENE BY THE SYSTEM $H_2SO_4 - H_2O$

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The absorption of olefins by sulfuric acid has been studied for a long time; however, owing to the complexity of the system olefin–water–acid, investigations devoted to the thermodynamics of this process are few in number [1-3].

The present work was devoted to a study of the thermodynamics of the complicated process of propylene absorption by aqueous sulfuric acid, during the course of which, as we have previously shown [4], alkylsulfuric acid and alcohol are formed thereby bringing about a sharp change in the properties of the original solution.

TABLE 1

Dependence of the Equilibrium Constant of the Alkylation Reaction on Concentration of the Original Acid; $t = 70°$ C, $K^{70°}_H = 3.27 \cdot 10^{-6}$ mole/liter · mm

H_2SO_4, %	$-H_0$	P_{eq} C_3H_6, mm Hg	C_{alk}, mole/liter	$C_{H_2SO_4}$, mole/liter	$K'_{alk} \cdot 10^{-1}$, (mole/liter)$^{-1}$	$\lg K'_{alk} + 0{,}732\, H_0$	Percent C_3H_6 in iso-$C_3H_7SO_4H$
62,65	4,43	233,0	0,14	9,56	0,1922	−1,959	18
67,70	5,13	191,7	0,641	10,345	1,000	−1,755	24
70,18	5,45	155,5	0,884	10,53	1,651	−1,772	27
74,03	6,02	81,2	1,37	11,214	4,601	−1,743	29

We investigated in detail the equilibrium of propylene absorption by sulfuric acid over an acid concentration range of 62.25-74.03% at temperatures of 70-95° and initial gas pressures of 300-600 mm Hg; the concentrations of alkylsulfuric acid and alcohol in the reaction mixture were determined. The experiments were carried out in a previously described glass circulation apparatus [4]. About 8 g of acid was used in an experiment. The volume of the system from which the propylene was absorbed was 2000 cc. Observations of the course of absorption were carried out by means of the drop in propylene pressure in the system, and the attainment of equilibrium was noted by lack of further pressure change. After saturation, the reaction mixture was rapidly diluted with a greater volume of water, and was then analyzed for alkylsulfuric acid and alcohol.

The alkylsulfuric acid was determined acidometrically, and the alcohol was determined by an oxidative titration method [5]. Knowledge of the equilibrium concentrations of alkylsulfuric acid and alcohol allowed us to determine the equilibrium constants for alkylation by sulfuric acid and for the hydration of propylene. These values have not been reported in the literature.

Equilibrium for the alkylation reaction

$$C_3H_6 + H_2SO_4 = \text{iso-}C_3H_7SO_4H \quad (I)$$

is conveniently characterized by the constant K'_{alk}, which may be expressed in terms of the experimentally determined values:

$$K'_{alk} = \frac{C_{\text{iso-}C_3H_7SO_4H}}{K_H P_{C_3H_6} C_{H_2SO_4}} = K_{alk} F, \quad (1)$$

where $F = f_{H_2SO_4} f_{C_2H_6} / f_{\text{iso-}C_3H_7SO_4H}$; K_{alk} is the thermodynamic equilibrium constant; f_i are activity coefficients; C_i are concentrations in moles per liter. Henry's law constant, K_H, was determined by extrapolation of literature data on the solubility of propylene in water [12] to the temperature of the experiment.

It follows from the data of Table 1 that K'_{alk} is related to H_0 as follows:

$$\log K'_{alk} = -0.732\, H_0 - 1.76. \quad (2)$$

The temperature dependence of K'_{alk} is shown in Table 2 (67.7% H_2SO_4).

TABLE 2

t, °C	P_{eq} C_3H_6, mm Hg	$K_H \cdot 10^4$, mole/liter	$C_{C_3H_6} \cdot 10^4$, mole/liter·mm	C_{alk} mole/liter	$C_{H_2SO_4}$, mole/liter	$K'_{alk} \cdot 10^{-3}$ (mole/liter)$^{-1}$	ΔS
70	191.7	3.27	0.627	0.641	10.345	1.001	−17.71
75	209.5	2.94	0.617	0.561	10.425	0.872	−17.52
80	213.0	2.66	0.566	0.483	10.503	0.813	−17.30
85	226.5	2.40	0.543	0.385	10.601	0.668	−17.32
90	225.4	2.16	0.487	0.302	10.684	0.581	−17.23
95	209.6	1.96	0.411	0.201	10.785	0.453	−17.35

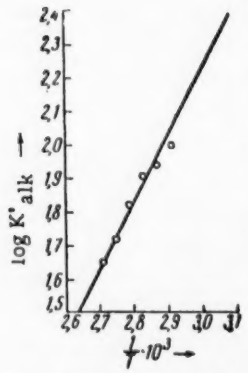

Fig. 1. Graph for calculation of the heat of the alkylation reaction.

Figure 1 presents a graph by which the heat of the alkylation reaction may be calculated. It was found the $\Delta H_{alk} = -9.2 \pm 0.2$ kcal/mole and $\Delta S = -17.4 \pm 0.2$ e.u.

Calculation of the equilibrium constant for the hydration of propylene in the liquid phase was of particular interest.

The formation of alcohol in an acid medium takes place according to the equation

$$C_3H_6 + H_2O + H_2SO_4 \rightleftharpoons \text{iso-}C_3H_7OH_2^+ + HSO_4^-, \quad (II)$$

which, in turn, is the sum of three equations:

$$C_3H_6 + H_2O \underset{k_{IV}}{\overset{k_{III}}{\rightleftharpoons}} \text{iso-}C_3H_7OH; \quad (III)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-; \quad (IV)$$

$$\text{iso-}C_3H_7OH + H_3O^+ \underset{k_V}{\rightleftharpoons} \text{iso-}C_3H_7OH_2^+ + H_2O. \quad (V)$$

The equilibrium of reaction (II) is conveniently characterized by the constant K'_{alc}, which may be expressed in terms of the experimentally determined values as

$$K'_{alc} = \frac{C_{\text{iso-}C_3H_7OH_2^+}}{C_{C_3H_6} a_{H_2O} h_0} = K_{alc} \frac{1}{k_{IV}} \frac{f_{C_3H_6}}{f_{\text{iso-}C_3H_7OH}}, \quad (3)$$

where h_0 is the acidity of the medium and K_{alc} is the equilibrium constant.

From the data available in the literature on the basicity of isopropyl alcohol [6] it follows that in 67.7% H_2SO_4 practically all of the alcohol is in the ionized form; i.e., the value of $C_{\text{iso-}C_3H_7OH_2^+}$ in Eq. (3) is equal to the concentration of all of the alcohol in the liquid phase as determined by analysis. Actually, analysis

of the gas phase over our system showed that the fraction of alcohol in the vapor phase did not exceed 10^{-4} of the total amount. In order to calculate the equilibrium constant K'_{alc} by means of Eq. (3), it is necessary to use the equilibrium values of a_{H_2O} and h_0^*, which differ substantially from the corresponding values for the original acid, as we have shown previously [11]. In calculating the equilibrium values, we used empirical formulas [11] relating a_{H_2O} and h_0^* to the alcohol content of the equilibrium system:

$$h_0^* = h_0 \frac{1 + 0.13C_{alc}}{1 + 0.52C_{alc}}, \quad a_{H_2O} = 55.51\ B\ (C_{alc} + \frac{P_{H_2O}/P_{SH_2O}}{B}), \tag{4}$$

where h_0 and h_0^* are, respectively, the values of the acidity of the original acid and acid with a concentration of C mole/liter of alcohol; P_{H_2O} and P_{SH_2O} are, respectively, the vapor pressure of water over the original acid and in the saturated space; it was found by extrapolation that at 70°, $B = 16.47 \cdot 10^{-2}$.

TABLE 3

Dependence of the Equilibrium Constant for the Hydration of Propylene in the Liquid Phase on the Acidity Function of the Original Acid. t = 70°, P_{SH_2O} = 233.7 mm Hg

H_2SO_4, %	$-H_0$	$h_0 \cdot 10^{-4}$	P_{eq} C_3H_6, mm Hg	P_{H_2O} mm Hg	C_{alc} mole/liter	a_{H_2O} mole/liter	$h_0^* \cdot 10^{-4}$	$K'_{alc} \cdot 10^3$ (mole/liter)$^{-1}$	log K'_{alc} − 0.319 H_0	Percent C_3H_6 in iso-C_3H_7OH
62,25	4,43	0,269	233,0	41,0	0,62	16,84	0,220	2,196	−1,246	80
67,70	5,13	1,51	191,7	23,0	1,80	23,97	0,960	1,230	−1,261	69
70,18	5,45	2,82	155,5	17,0	2,38	27,78	1,650	1,022	−1,253	70
74,03	6,02	10,22	81,2	9,0	3,38	33,04	5,334	0,721	−1,222	67

It follows from the data of Table 3 that the value of log K'_{alc} is related to H_0 by the equation:

$$\log K'_{alc} = 0.319\,H_0 - 1.245. \tag{5}$$

The temperature dependence of K'_{alc} is shown in Table 4.

TABLE 4

Dependence of the Equilibrium Constant for the Hydration of Propylene in the Liquid Phase on Temperature. 67.7% H_2SO_4

t, °C	P_{eq} C_3H_6 mm Hg	$K_H \cdot 10^6$, mole/liter·mm	$C_{C_3H_6} \cdot 10^3$, mole/liter	P_{H_2O}, mm Hg	P_{SH_2O}, mm Hg	$B \cdot 10^2$ from Eq. (4)	C_{alc}, mole/liter	a_{H_2O} mole/liter	$h_0 \cdot 10^{-4}$	$h_0^* \cdot 10^{-4}$	$K'_{alc} \cdot 10^3$ (mole/liter)$^{-1}$	ΔS
70	191,7	3,27	0,627	28,0	233,7	16,47	1,80	23,97	1,51	0,960	1,239	−23,32
75	209,5	2,94	0,617	27,5	294,4	22,11	1,25	20,52	1,41	0,993	0,994	−23,49
80	213,0	2,66	0,566	35,5	355,1	27,75	1,32	25,88	1,35	0,9172	0,9828	−23,38
85	226,5	2,40	0,543	46,5	440,4	37,25	1,30	32,74	1,26	0,898	0,851	−23,53
90	225,4	2,16	0,487	58,0	525,76	46,76	1,32	40,38	1,20	0,834	0,803	−23,51
95	209,6	1,96	411	73,3	633,9	62,77	1,29	51,36	1,12	0,7826	0,780	−23,41

Figure 2 presents a graph for the calculation of the heat of hydration. It was found that $\Delta H_{alc} = -3.7 \pm 0.3$ kcal/mole and $\Delta S = -23.44 \pm 0.12$ e.u.

It is apparent from Tables 1 and 3 and Fig. 3 how the fraction of propylene converted to alcohol and alkylsulfuric acid changes with the concentration of the original H_2SO_4; this is in agreement with the literature data [2, 3].

Table 5 presents values of the equilibrium constant for the over-all absorption of propylene, $K_{ov} = \Delta P_\infty / P_{eq}$,

where ΔP_∞ is the equilibrium pressure drop in the system, and P_{eq} is the equilibrium pressure. K_{ov} is related to the alkylation constant K'_{alk} and the alcohol-formation constant K'_{alc} by the equation:

$$K_{ov} = \frac{K_H RTV_{acid}}{2000}(K'_{alc} a_{H_2O} h_0 + K'_{alk} C_{H_2SO_4}), \quad (6)$$

where V_{acid} is the volume of acid in liters. It was found that the over-all heat $\Delta H_{ov} = -8.7 \pm 0.8$ kcal/mole and $\Delta S = -15.14 \pm 0.3$ e.u.

By means of these data it is possible to calculate a series of interesting values. Knowledge of the heat of alkylation of propylene by sulfuric acid makes it possible to calculate the heat of formation of isopropylsulfuric acid from the elements (ΔH_f) iso-$C_3H_7SO_4H$.

$$(\Delta H_f)_{\text{iso-}C_3H_7SO_4H} = \Delta H_{alk} + (\Delta H_f)_{C_3H_6(l)} + (\Delta H_f)_{H_2SO_4(2.68)},$$

where (ΔH_f) $C_3H_6(l)$ is the heat of formation of liquid propylene; (ΔH_f) $H_2SO_4(_{2.68})$ is the heat of formation of sulfuric acid at a mole ratio of water to sulfuric acid in the solution of 2.68 : 1 ≈ 3.1; this value is −205.6 kcal/mole [8]:

(ΔH_f) iso-$C_3H_7SO_4H$ = (−9.2 + 0.48 − 205.6) kcal/mole = − 214.32 kcal/mole.

By means of the value obtained for the heat of formation of the protonized form of the alcohol, it is possible to calculate by difference the heat of protonization of isopropyl alcohol: $\Delta H_v = \Delta H_{alc} - \Delta H_{III}$.

The heat of reaction (III), ΔH_{III}, was found with the aid of the values from the tables:

$$\Delta H_{III} = (\Delta H_f)_{\text{iso-}C_3H_7OH(l)} - (\Delta H_f)_{H_2O(l)} - (\Delta H_f)_{C_3H_6(l)};$$
$$\Delta H_{III} = (68{,}4 - 0{,}5 - 76{,}6)\text{kcal/mole} = -8{,}7 \text{ kcal/mole}.$$

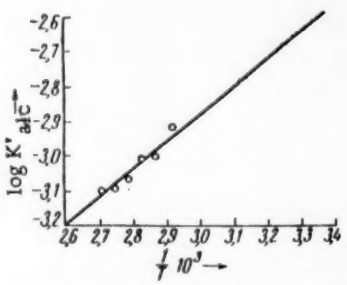

Fig. 2. Graph for the calculation of the heat of hydration.

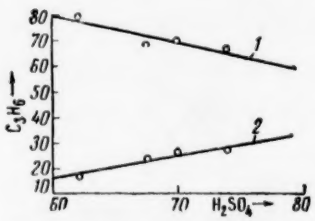

Fig. 3. Dependence of the percentage conversion of C_3H_6 to iso-C_3H_7OH (1) and to iso-$C_3H_7SO_4H$ (2) on acid concentration.

whence the heat of protonization of isopropyl alcohol is

$$\Delta H_v = (-3{,}7 + 8{,}7) \text{ kcal/mole} = 5 \text{ kcal/mole}.$$

Our value for the heat of protonization of isopropyl alcohol is close to the heat of protonization of methyl alcohol, $\Delta H = 4.6$ kcal/mole, calculated from the data of Smith [10].

TABLE 5

Dependence of the Equilibrium Constant for the Over-all Absorption of Propylene on Temperature. 67.7% H_2SO_4.

t, °C	Acid, g	P_0 C_3H_6, mm, Hg	ΔP_∞ mm Hg	P_{eq} C_3H_6, mm Hg	K_{ov}	$K_{red} = \frac{K_{ov} \cdot 2000}{\text{g acid}} 10^{-3}$
70	7,64	322,5	130,8	191,7	0,682	1,783
75	7,79	318,5	109,0	209,5	0,520	1,335
80	7,87	313,5	100,5	213,0	0,472	1,200
85	7,53	316,8	90,3	226,5	0,398	1,054
90	7,34	291,0	65,6	225,4	0,291	0,794
95	7,16	269,0	59,6	209,6	0 285	0,798

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RADIATION OXIDATION OF LEUCO BASES TO KETONES IN THE ABSENCE OF OXYGEN

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Radiation oxidation reactions in organic systems due to molecular oxygen are well known. However, in analogy with aqueous solutions, one might expect the oxidation of dissolved substances in organic liquids under the action of radiation in the absence of molecular oxygen due to radical and molecular radiolysis products of the solvent. In organic compounds, these products are much more diverse than in water, but it is not in all cases that they have quite sharply expressed oxidizing properties.

Dainton et al. [1] described and used the reduction of trivalent iron in various organic liquids under the action of radiation for determining free radicals formed. The literature contains no data on analogous oxidation reactions. They are most likely to appear in cases where the solvent contains functional groups with readily reduced oxygen, such as carbonyl groups, nitro groups, etc.

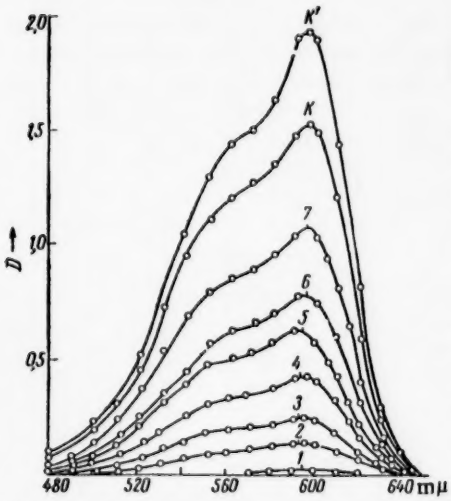


Fig. 1. Absorption spectra of Crystal violet and the radiation conversion product of its leuco base: 1) $5 \cdot 10^{-3}$ M solution of LCV in acetone; 2-7) irradiated solutions of LCV ($5 \cdot 10^{-3}$ M); doses: 2) $2.5 \cdot 10^{16}$; 3) $5 \cdot 10^{16}$; 4) $7.9 \cdot 10^{16}$; 5) $1.2 \cdot 10^{17}$; 6) $1.5 \cdot 10^{17}$; 7) $2.1 \cdot 10^{17}$ ev/cc; K and K') $1 \cdot 10^{-6}$ and $1.2 \cdot 10^{-6}$ M solutions of CV.

Our investigation of the action of ionizing radiations on nitrogen-saturated solutions of the leuco base of Crystal violet (LCV) in acetone and methyl ethyl ketone showed that there is actually oxidation of the leuco base in these systems.

Figure 1 gives the spectra of the radiation conversion product of LCV with increasing doses (curves 2-7) and the spectrum of CV in the same solvent (curve K) for comparison. The intense color of the triphenylmethane dye solutions ($\epsilon \sim 10^5$) made it easy to follow the initial stages of the process; the Lambert-Beer law was obeyed at all concentrations of the dyes formed up to 10^{-4} M.

When the air had been displaced by nitrogen, solutions of the leuco base in carefully purified ketone were sealed off in tubes 18-20 mm in diameter and 100-120 mm long, which made it possible to carry out the radiation and subsequent determination of the optical density with an SF-2M recording spectrophotometer without the solution coming in contact with air. The solutions were subjected to the action of ^{60}Co γ-rays, 80 kv_{max} x-rays, and polonium α-particles. In the first two cases the dose strength was determined by ferrous sulfate dosimetry with appropriate correction for the ketone and for the α-particles; it was calculated from the amount of polonium perchlorate introduced.

Figure 2 shows for all three forms of radiation the increase in the concentration of dye formed with increase in the energy absorbed in $5 \cdot 10^{-3}$ M LCV, irradiated at 25° C.

As the figure shows, the amount of dye increased in direct

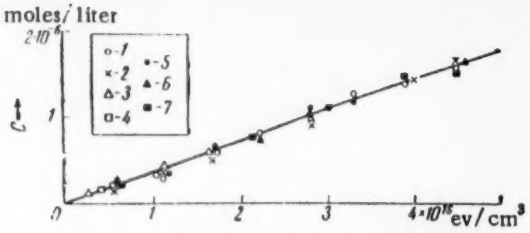


Fig. 2. Action of x-radiation, γ-radiation, and α-particles on LCV solutions at various dose strengths: 1) α-particles, 2) 0.05 r/sec, 3) 0.4, 4) 5.6, 5) 0.1, 6) 1.0, 7) 1.6 r/sec; 2-4) ^{60}Co γ-radiation; 5-7) x-radiation.

proportion to the dose. The yield G = 2.06 ± 0.03 molecules/100 ev was the same for acetone and methyl ethyl ketone and depended neither on the nature of the radiation nor on the dose strength. An investigation of the action of x-radiation over the range -85° to +50° showed that the yield was also independent of temperature and remained equal to 2.0 ± 0.1. The relation of yield to LCV concentration is shown in Fig. 3 for acetone and methyl butyl ketone.

Over the range of concentrations examined (10^{-3} - 10^{-2} M), the radiation conversions of the dissolved substance were caused solely with radiolysis products of the solvent and not by the direct action of radiation. Under normal experimental conditions, observed chemical effects of short-lived radical products cease when irradiation ceases, while stable molecular products may react after the end of irradiation.

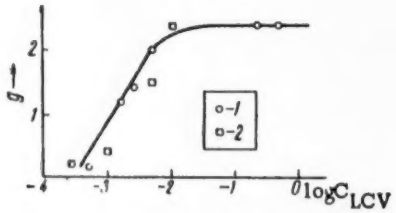


Fig. 3. Relation of the yield of dye formed to the concentration of Crystal violet leuco base for acetone (1) and methyl butyl ketone (2).

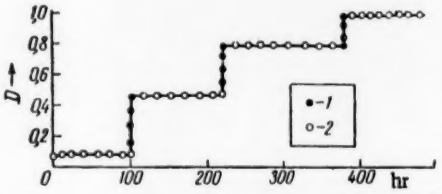
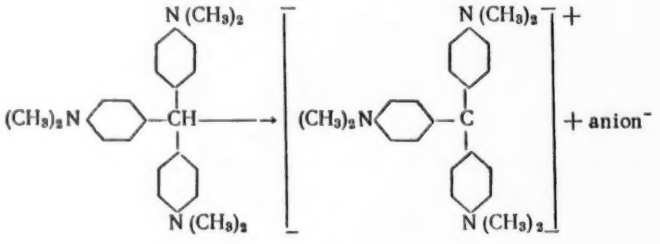


Fig. 4. Change in optical density of a $5 \cdot 10^{-3}$ M solution of LCV during irradiation and after irradiation; 1) irradiation; 2) after irradiation.

Figure 4 shows the change in the optical density of a solution during the absorption of various doses and after irradiation had stopped. A solution which had absorbed not more than ~10^{17} ev/cc remained unchanged over a long period. This indicated that the radiation oxidation of LCV was caused by radical radiolysis products of the ketones. A radical mechanism is also indicated by the concentration dependence of the yield (Fig. 3), which shows a characteristic plateau at 10^{-3} - 10^{-2} M, corresponding to complete trapping of available radicals. From the fact that the oxidation yield is independent of the nature of the radiation (ionization density) it follows that in contrast to water, in organic liquids, intratrack interactions of radicals do not play a substantial part. This is also indicated by the fact that the yield of gaseous radiolysis products of hydrocarbons is independent of the ionization density [2]. At doses of more than $3 \cdot 10^{17}$ ev/cc, the yield of CV formation began to fall and the solution was gradually decolorized after irradiation had been stopped.

An investigation of the action of γ-radiation on acetone and deuteroacetone [3] indicates that among the primary radiolysis products, the main role is played by the radicals $\dot{C}H_2COCH_3$, $\dot{C}H_3$ and $\dot{C}H_2COCH_3$; among these the radical $CH_3\dot{C}O$ should readily effect an oxidation reaction of the type $CH_3\dot{C}O + RH \longrightarrow CH_3CHO + R$.

The conversion of the colorless leuco base into the dye



(1)

is a two-stage oxidation process. In view of the low probability of a second interaction with one particle, it may be assumed that with a comparatively high yield G~2-2.5, it is only the first act, i. e., abstraction of a hydrogen atom from the central carbon of LCV, which is a radiation process, and that it is affected by the radical $CH_3\dot{C}O$ according to the reaction:

$$[(CH_3)_2NC_6H_4]_3CH + CH_3\dot{C}O \rightarrow [(CH_3)_2NC_6H_4]_3\dot{C} + CH_3CHO. \quad (2)$$

The analogous reaction

$$CH_3\dot{C}O + CH_3COCH_3 \rightarrow CH_3CHO + \dot{C}H_2COCH_2 \quad (3)$$

may explain the formation of acetaldehyde, the yield of which in the radiation of pure acetone in the absence of oxygen G = 2.5 ± 0.2 molecules/100 ev. The aftereffect corresponding to doses above $\sim 3 \cdot 10^{17}$ ev/cc is caused by the accumulated molecular radiolysis products. Separate experiments showed that acetone irradiated in the absence of oxygen acquires the power to decolorize CV. On the other hand, it was established that molecular radiolysis products of acetone, acetaldehyde and acetalacetone, decolorize a solution of dye in unirradiated acetone.

As acid was absent from an irradiated solution of LCV, the observed formation of cation must have proceeded through the transfer of an electron from the aminotriphenylmethyl radical to solvent or from a polar impurity, for example water, with the formation of the corresponding anion [4].

Analogous oxidation reactions with different yields occur during the action of radiation on solutions of leuco bases of other triphenylmethane dyes (Malachite green, Brilliant green, and Ethyl violet). The radiation oxidation to ketones in the absence of oxygen was determined by the presence of the carbonyl group. Substantially different processes were possible in solvents with other functional groups. Thus, for example, LCV was hardly oxidized in ethanol: at an LCV concentration of 10^{-3} M, G (CV) = 0.066 instead of G (CV) = 1.2 in acetone. At the same time, during irradiation in alcohol there was reversible reduction of Methylene blue to the leuco base, which did not occur in acetone.

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DETERMINATION OF THE STRUCTURE OF SOME DIHYDROFURAN DERIVATIVES BY RAMAN SPECTRA

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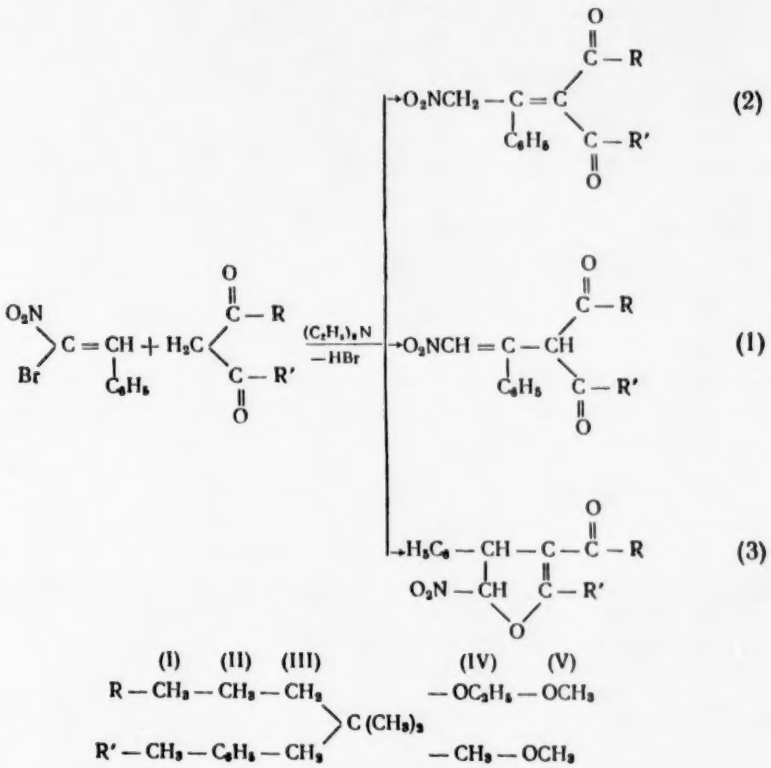
The reaction of β-bromo-β-nitrostyrene with substances containing active methylene groups (acetyl- and benzoylacetone, dimedon , and acetoacetic and malonic esters) in the presence of triethylamine yielded products (I-V), to which three different isomeric formulas could be assigned in each case:



(I) (II) (III) (IV) (V)

R — CH_2 — CH_2 — CH_2 — OC_2H_5 — OCH_3

R′ — CH_2 — C_6H_5 — CH_2 — CH_2 — OCH_3

Products of type (I) could have arisen as a result of the addition of the methylene component to β-bromo-β-nitrostyrene and subsequent dehydrohalogenation; products of type (2) should be regarded as products from the

isomerization of (I), in which the hydrogen atom of the methyne group is activated by two carbonyl residues; the formation of (3) was explained by enolization of the addition products and subsequent elimination of hydrogen bromide. We cannot exclude the possibility of the migration of the double bond in the dihydrofuran ring into the 3-4 position. Available chemical methods were found to be inadequate for a conclusive choice of one of the possible formulas.

An investigation of the band intensities in the Raman spectrum made it possible to establish the structure of the reaction products unequivocally.

We previously showed that the band intensities in the Raman spectra of a nitro group, double bond, and benzene ring, respectively, change up to three orders in relation to the nature of their conjugation [1].

Formulas of type (1) contained a conjugated system of nitrostyrene, formulas of type (2) contained the system of cinnamic acid or benzylidene ketones and an unconjugated nitro group, while the dihydrofuran derivatives (3) had the residue of acrylic acid or vinyl ketones and an unconjugated benzene ring and nitro group.

The spectra of products I-V showed frequencies of a nitro group, benzene ring, and double bond and the intensities of these coincided with or were close to the intensities of an unconjugated nitro group, an unconjugated benzene ring, and a double bond conjugated with a carboxyl or carbonyl group, which are present in the proposed formula (3) (Table 1). Thus, the products from the reaction of β-bromo-β-nitrostyrene with the above active methylene components undoubtedly had a dihydrofuran structure.

TABLE 1

Substances	Intensities*		
	$-C_6H_5$	$-CH=CH-$	$-NO_2$
$C_6H_5-CH=CH-NO_2$	2,4	4,3	9
$C_6H_5-CH=CH-COOH$	0,7—1,0	1,2	—
$CH_2=CH-COOH$	—	0,04	—
$C_6H_5-CH_3$	0,02	—	—
CH_3NO_2	—	—	0,02
I	0,01—0,02	0,1—0,2	0,01—0,02
II	1,0	0,5—1,0	0,01—0,02
III	0,06	0,15—0,3	0,01—0.02
IV	0,035	0,08—0,15	<0,01—0,02
V	—	0,1	<0,01—0,02

*In arbitrary scale units.

The high values of the band intensities of the benzene ring and the double bond in product II, which were close to the corresponding values in cinnamic acid, indicated that it was formed as a result of enolization of the carbonyl group adjacent to the benzene ring and not the methyl group. The certain increase in the band intensities of the double bond in products I-V in comparison with acrylic acid is evidently explained by conjugation of this bond with the unshared pair of electrons of the oxygen of the furan ring.

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*Original Russian pagination. See C.B. translation.

REACTION OF NAPHTHALENE WITH SULFUR

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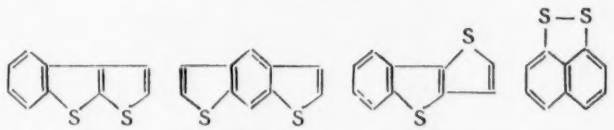
In 1911 M. M. Lanfry passed naphthalene and sulfur vapor through a red-hot iron tube and obtained a small amount of a ruby red substance with the composition $C_{10}H_6S_2$ and m. p. 118.5°. He assigned the structure of thienothionaphthene I or II to this compound on the basis of qualitative reactions and the empirical formula [1]. It was later suggested [2] that the structure of thienothionaphthene III should be assigned to this substance.



(I) (II) (III) (IV)

However, in 1957 Indian investigators [3] synthesized compounds I, II, and III by a method which left no doubt as to their structure and established that none of them was identifical with the substance formed by the reaction of naphthalene with sulfur. Thus, the problem of the structure of the interesting product obtained by M. M. Lanfry remained unsolved up to the present. On examining the literature, we were attracted by the fact that 1,8-napthalene disulfide (IV), which was synthesized in 1928 by S. Smiles and W. B. Price [4] and has the same empirical formula $C_{10}H_6S_2$, is very similar in physical properties (a red substance with m. p. 116° and according to the data in [5] 119°) to the substance isolated by M. M. Lanfry.

As the formation of 1,8-napthalene disulfide by the reaction of napthalene with sulfur seemed more probable to us than the formation of thienothionaphthene, we repeated the work of M. M. Lanfry for a direct comparison of these two compounds. It should be noted that in his article, M. M. Lanfry did not give experimental details (ratio of starting naphthalene and sulfur, reaction temperature, and method of isolating the substance from the mixture obtained). We passed naphthalene and sulfur vapors in a ratio of 1 : 3 through a red-hot iron tube (600-700°). This yielded a condensate which contained a large amount of unchanged naphthalene that was steam distilled. Repeated recrystallization of the residue from alcohol and subsequent vacuum sublimation (55° at 2 mm Hg) yielded the expected red crystalline product with m. p. 116-117°. 1,8-Naphthalene disulfide was synthesized by the method described in the literature [4-6], starting from 1,8-naphthylaminosulfonic acid and had m. p. 118-119°. When these two compounds were compared, it was found that the melting point of a mixture was not depressed and their infrared and ultraviolet absorption spectra (see Figs. 1 and 2) were completely identical.

Thus, it may be considered as established that 1,8-naphthalene disulfide is formed when naphthalene and sulfur vapors are passed through a red-hot iron tube.

An interesting property of 1,8-napthalene disulfide is its capacity to give clear positive reactions for a thiophene ring (indophenine reaction with isatin and Liebermann's test with phenanthrenequinone), which led M. M. Lanfry to the wrong conclusion on the structure of the compound he obtained.

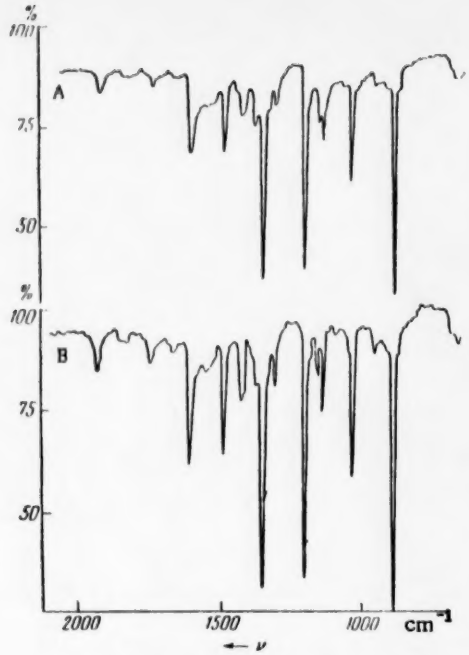


Fig. 1. Infrared absorption spectrum of the substance obtained by M. M. Lanfry's method (A) and 1,8-naphthalene disulfide (B).

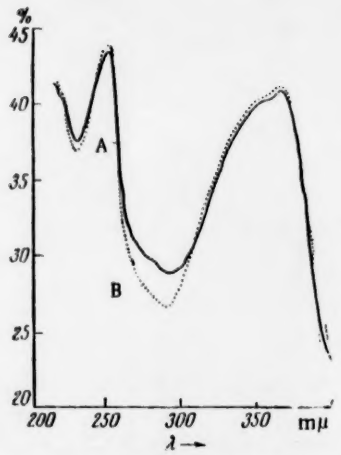


Fig. 2. Ultraviolet absorption spectrum of the substance obtained by M. M. Lanfry's method (A) and 1,8-naphthalene disulfide (B).

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EQUILIBRIUM IN THE TITANIUM – TIN SYSTEM

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A considerable number of investigations have been devoted to the chemical reaction of Ti with Sn [1-11].

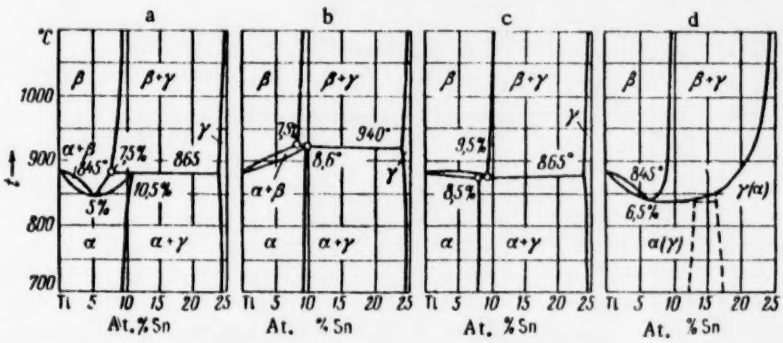

Fig. 1. Variants of the phase diagram of the Ti–Sn system according to the data of various authors: a) [6], b) [7], c) [8], d) [9, 10].

The data obtained by different authors differs sharply and as a result of this, four fundamentally different variants have been put forward for the equilibrium between α-Ti and the γ-phase (Fig. 1 according to the data in [6-11]).

By analyzing the data of [6-11] from the point of view of the reliability of the experimental procedures used, the purity of the starting materials, and the duration of the homogenation of the alloys for them to reach the equilibrium state, it may be concluded that the alloy samples closest to equilibrium were apparently obtained by M. K. McQuillan [10], who fired them at 880° for 5500 hr. In the other work the firing time was much less. M. K. McQuillan considered that a continuous series of solid solutions is formed between α-Ti and Ti_3Sn.

It should be noted that α-Ti and Ti_3Sn have similar crystal structures [4, 5]. The atomic radii of α-Ti and γ-phase in the corresponding lattices for the coordination number 12 differ by less than 8%, which satisfies the rules of I. I. Kornilov [12] and Hume-Rothery [13].

The present work was carried out to finally solve the question of the nature of the equilibrium in the Ti–Sn system between α-Ti and the γ-phase and to construct the equilibrium phase diagram over the range of concentrations 0 to 25 at. % Sn. In planning the work, we considered the experience and results of the investigations presented in [6-11].

A comparative assessment of the methods of preparing alloys based on Ti for an investigation of phase diagrams [14] showed that the most suitable method is induction fusion in a suspended state [15].

This method was therefore chosen for preparing the alloys.* Alloys with the following compositions (according to chemical analysis data) were prepared: 0.83, 2.12, 4.35, 5.28, 6.52, 7.78, 10.1, 14.9, 18.1, 22.0, and 25 at. % Sn. The starting materials were Ti of 99.9% purity (σ_B = 37 kg/mm^2) and 99.99% Sn.

Microscopic analysis of cast samples showed that alloys containing up to 14.9% Sn inclusive were single-phase. Alloys with 18.1 and 22.0% Sn contained small layers of a second phase. For equilibration of the alloys, after 10-20% preliminary deformation, they were annealed at 850° in a vacuum of 10^{-4} mm.

Microscopic analysis of the alloys after annealing for 1500 hr showed that the layers of the second phase in alloys with 18.1 and 22.0 at. % Sn became considerably thinner.

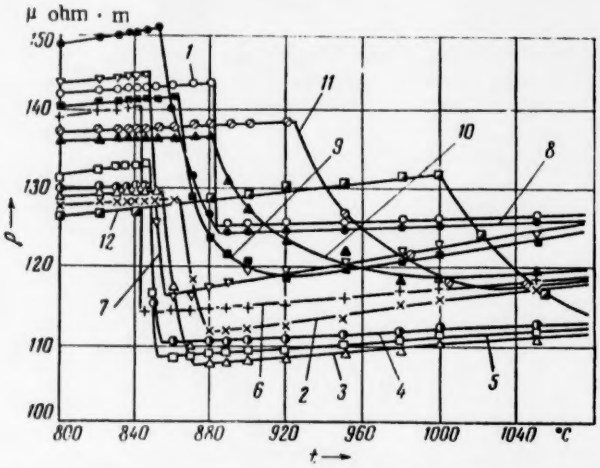

Fig. 2. Temperature dependence of the electrical conductivity of Ti–Sn alloys. Sn content of alloy (in %): 1) pure Ti, 2) 0.82,3) 2.12, 4) 4.35, 5) 5.28, 6) 6.50, 7) 7.78, 8) 10.1, 9) 12.0, 10) 14.9, 11) 18.1, 12) 22.0.

Alloys containing 4.35, 5.28, 6.52, and 7.78 at. % Sn had an α' structure. The other alloys had a polyhedral structure. In connection with this, all the alloys were again subjected to 10-20% deformation and reannealed for 1200 hr at 800°.

Subsequent investigation of the microstructure showed that all the alloys were single phase and had an α(γ) polyhedral structure; this indicates the presence of a continuous series of solid solutions between α-Ti and the γ-phase. For determining the upper temperature boundary of the α(γ)-phase region, we investigated the temperature dependence of the specific electrical conductivity of the alloys ρ [16], which was measured by a noncontact method [17] in a vacuum of 10^{-4} mm on the apparatus described in [18]. The measurements were carried out at 5-10° intervals over the range 800-900°. The results of the measurements are given in Table 1.

For all the alloys, ρ first increases linearly with a rise in temperature (the values of α_t for this temperature range are given in Table 2) and then the rate of increase of ρ with temperature decreased. A sharp fall in ρ was observed at the phase transition. The values of ρ at adjacent temperatures between which the phase transition occurred are linked by brackets in Table 1.

For alloys for which the α→β transition occurs over a temperature range, it was possible to observe the temperature of the transition from the α + β to the β region as ρ(β) increases slowly with a rise in temperature, while ρ(α + β) falls sharply; this is evidently connected with the rate of the phase transition, which is large in the given

* In all the previous investigations, the alloys were prepared by fusion of the components in an arc furnace with a water-cooled copper bottom plate and an unconsumable electrode.

case as the temperature range of the ($\alpha + \beta$) region is very narrow for the alloys investigated.

TABLE 1

Electrical Resistance ρ of Ti–Sn Alloys at Different Temperatures (μohm·cm)

Temp. °C	Sn content of alloy in at.%												
	0	0,83	2,12	4,35	5,28	6,52	7,78	10,1	12,0	14,9	18,1	22,0	25,0
20	45,5	57,8	70,0	85,0	93,0	101,5	113,0	116,0	116,0	111,0	101,0	84,0	71,0
120	65,4	72,5	84,1	95,3	100,2	109,0	118,6	119,0	119,5	116,0	106,2	91,5	80,3
200	78,5	87,0	93,6	105,5	108,0	113,5	124,0	124,0	122,5	119,7	111,0	98,5	89,4
300	94,4	100,0	105,0	114,6	114,3	119,5	130,1	128,5	127,0	124,8	116,2	105,3	97,5
400	110,5	109,0	114,2	119,5	120,0	123,8	135,0	136,0	133,0	126,8	120,8	111,5	105,0
500	122,6	117,0	120,3	122,3	122,0	129,5	138,0	138,0	137,1	130,2	127,2	117,3	112,5
600	132,0	121,2	123,1	125,8	125,3	132,3	140,5	142,3	138,5	132,4	129,5	121,1	118,5
700	139,1	125,0	127,8	128,7	129,0	135,7	142,5	145,0	139,8	134,5	132,1	125,4	122,1
750	142,1	128,0	128,8	129,1	130,5	137,3	144,0	147,0	140,5	135,2	133,4	127,0	123,5
800	143,0	128,0	129,3	129,3	132,0	139,4	144,3	149,7	140,8	135,4	134,0	128,8	125,1
820	143,4	128,3	129,5	129,7	133,0	140,0	144,2	150,0	141,0	135,1	135,2	129,2	
830	143,2	128,1	129,5	129,7	133,5	140,0	144,5	150,3	141,2	135,6	135,4	129,5	
835	143,3	128,3	129,3	130,1	133,4	140,3	145,0	150,4	141,7	135,5	136,0	130,0	
840	143,2	128,0	129,2	130,3	134,0	140,5	145,1	150,5	142,0	135,3	136,1	130,3	
845	143,3	128,2	129,4	130,3	134,0	114,5	145,3	150,4	142,0	135,8	136,6	131,1	
850	143,5	128,2	129,7	115,1	115,0	114,3	125,5	151,0	142,3	136,0	137,0	131,4	128,3
860	143,5	129,0	117,5	110,8	108,5	114,6	117,5	140,1	142,8	136,6	137,2	131,0	
870	144,2	118,7	110,0	109,7	108,5	114,9	118,0	132,2	129,0	136,3	137,1	131,5	
880	144,3	112,5	108,0	109,5	108,8	114,8	119,0	127,0	124,0	136,4	137,5	131,5	
890	125,4	112,7	108,4	109,8	109,0	115,0	119,5	125,1	122,0	131,5	137,5	131,7	
900	125,5	113,0	108,5	110,2	109,3	115,2	120,1	125,2	120,3	127,2	137,8	132,0	
920	125,8	113,5	108,7	110,2	109,5	115,3	120,5	125,2	119,0	124,5	137,7	132,2	
950	125,6	114,0	109,1	111,4	110,0	116,0	121,3	125,5	119,0	120,8	126,1	132,1	
980	125,8	115,2	109,5	111,7	110,5	116,8	121,5	126,1	120,5	118,0	121,3	132,3	
1000	126,1	116,0	110,4	112,4	111,3	117,0	121,8	126,3	122,5	118,2	117,5	132,5	130,2
1050	126,3	116,9	111,0	113,0	112,0	118,1	122,3	127,0	123,1	119,0	117,0	118,0	
1100	126,5	117,5	111,3	113,3	115,1	119,5	123,1	129,2	124,5	118,8	117,4	117,5	
1150	127,2	118,5	112,0	115,0	115,8	120,0	123,5	130,0	125,0	120,0	119,0	119,0	133,0

TABLE 2

Temperature Coefficient of Electrical Resistance and Phase Transition Temperatures in Ti–Sn Alloys

	Sn content of alloy in at.%												
	0	0,83	2,12	4,35	5,28	6,52	7,78	10,1	12,0	14,9	18,1	22,0	25,0
Temp. range, °C	20–400	20–300	20–300	20–250	20–250	20–200	20–200	20–200	20–200	20–200	20–200	20–200	20–200
α_t, μohm·cm/deg	0,178	0,161	0,132	0,113	0,083	0,068	0,061	0,044	0,036	0,055	0,067	0,081	0,105
Transition t, °C $\alpha \rightarrow \alpha + \beta$, $\alpha \rightarrow \beta$ or $\alpha \rightarrow \beta + \gamma$	882	865	855	847	845	842	845	850	860	880	925	1000	—
Transition t, °C $\alpha + \beta \rightarrow \beta$ or $\beta + \gamma \rightarrow \beta$	—	880	875	855	850	—	855	880	—	—	—	—	—

Figure 2 gives the relations of ρ to t over the range 800-1050°. The phase transition temperatures for the alloys investigated were determined from the sharp breaks in these curves (see Table 2).

Figure 2 shows that for alloys with 5.28 and 7.78 at. % Sn, the transition from the α to the β region occurred over a temperature range, while the alloy with 6.52 at.% Sn, which lies between them, underwent an isothermal conversion at 842° or, in any case, the conversion range was less than 5°, as is indicated by the sharp change in ρ and the absence of intermediate points on the descending branch of the curve for the relation of ρ to t.

Figure 3 gives the concentration dependences of ρ at 20, 200, and 300°, and α_t. As this figure shows, the composition dependences of ρ are characterized by smooth curves with a maximum corresponding to ~12% Sn. The concentration dependence of α_t is characterized by a smooth curve with a minimum, which also corresponds to ~12% Sn (Fig. 3 b). The nature of the dependences of these properties are typical of systems with a continuous series of solid solutions [19].

For a more accurate determination of the boundary between the β and β + γ and also β + γ and γ phase regions, alloys were annealed for 200 hr at 900, 1000, and 1100°. Microscopic analysis of samples quenched at the given temperatures showed that all the alloys over the concentration range from 0.83 to 10.1% Sn had an α' structure; alloys with 12.0, 12.9, 18.1 and 22.0% Sn had an α' + γ structure.

Determinations of the melting points of the alloys, which were carried out by the method of G. A. Meerson [20], confirmed the data in [6-10].

On the basis of the experimental material obtained, we constructed the equilibrium variant of the Ti–Sn diagram presented in Fig. 4. From this figure it follows that there is a continuous series of solid solutions between α-Ti and the γ-phase. The addition of Sn reduces the temperature of the allotropic conversion of Ti to a minimum at 842° and 6.52 at. % Sn and then increases it again.

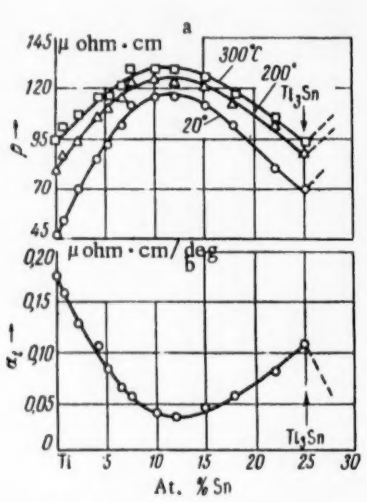

Fig. 3. Relation of the electrical resistance (a) and the temperature coefficient of the electrical resistance (b) to the composition of Ti–Sn alloys.

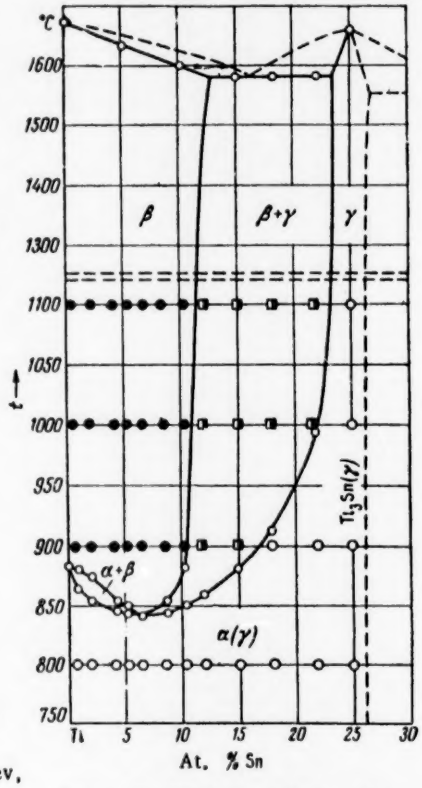

Fig. 4. Equilibrium variant of the Ti–Sn phase diagram according to data obtained in the present work.

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EXTRACTION WITH THE PARTICIPATION OF THREE CHELATE FORMERS

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In studying the extent of mixed chelate formation by the method of extraction, we observed interesting cases of the extraction of colored compounds caused by the simultaneous presence of three different chelate formers.

As chelate forming reagents we used 4-nitro-2, 2'-dihydroxy-5-methylazobenzene (I), 4-nitro-2, 2'-dihydroxy-4'-methyl-5'-isopropylazobenzene (II), 8-hydroxyquinoline (III), 2-methyl-8-hydroxyquinoline (IV), 5-methyl-8-hydroxyquinoline (V), mono-n-butyl phosphate (VI), di-n-butyl phosphate (VII), N-nitrosophenylhydroxylamine (VIII), acetoacetic ester (IX), 2-carbethoxycyclopentanone (X), 2-hydroxyacetophenone (XI), and benzoylsalicoylmethane (XII).

Chloroform was used for the extraction. The initial concentration of cations in the aqueous phase was 40 μg/ml. Not less than four moles of each reagent was added for each g-ion of metal. Control experiments in which either the cation or one of the three reagents in turn was omitted were carried out under identical conditions for comparison.

In the following cases there was extraction of colored compounds (pink or violet) at pH 10-12 when three reagents were present simultaneously (the extracts were colorless in all control experiments): scandium—combinations of reagents II, VII, and IX (or X); yttrium and rare earth elements—combinations of I, IV, XII; I (or II), IV (or V), VI; II, III (or IV, or V), VII; II, III (or V), XI (or X); II, VII, IX (or X); thorium—combinations of I, V, VIII; I, VII, XI; II, IV, VIII; II, III (or IV, or V), VII; II, VII, IX (or X).

In contrast to 8-hydroxyquinoline (III) and 5-methyl-8-hydroxyquinoline (V), which are similar in structure, 2-methyl-8-hydroxyquinoline (IV) did not produce the extraction of colored complexes in combinations with II and IX in the case of rare earth elements and with I and VIII in the case of scandium. Similar phenomena occurred in the case of thorium in binary combinations with I or II, respectively, with reagents IV, III, and V. In contrast to 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline is unable to precipitate aluminum [1] and forms an extractable chelate complex with it [2], which may be connected with steric hindrance to chelate formation [3]. This is also probably the reason for the anomalous behavior of 2-methyl-8-hydroxyquinoline which we observed.

At lower pH values, there was sometimes a change from the orange-yellow color of reagents I or II to orange-red or red of the complexes extracted. For example, yttrium, rare earth elements, and thorium gave this change with combinations of reagents I, III (or IV or V), and VI in the pH range 6-8.

There were also cases when the presence of the third chelate former produced both an increase in the intensity of the color and some deepening (in comparison with binary combinations). This was observed for zirconium on addition of III or V to the combination II + VIII (at pH 8-12); for thorium, on addition of III, IV, or V to the combination II + VIII (pH 6-12); for yttrium and rare earth elements, on addition of IX, X, or XI to the combi-

nation I + VII and III, IV, or V to the combination II + XI (pH 6-12).

Special experiments showed that the ratio of the reagents had a substantial effect of the extractability of the corresponding colored compounds, especially at relatively low concentrations. Thus, for example, by reducing the concentration of reagent IV in the system of reagents I, IV, and XII at pH 10-12, it was possible to improve considerably the selectivity of the extraction of colored compounds of rare earth elements. In many other cases it was also possible to find conditions for the selective extraction of compounds formed by elements with similar properties and the same valence. For example, in contrast to zirconium, thorium forms colored extractable complexes with combinations of reagents I, VII, and XI and II, V, and VII, while yttrium and rare earth elements, in contrast to scandium, form such complexes with I, VII, and IX (or XI) at pH 10-12.

As regards the extraction mechanism, it must be assumed that under the conditions investigated, reagents I and II form chelate compounds through at least two donor groups as the extracts have the color of the deprotonized form of the corresponding reagent. In other words, in the given case there is not the coextraction of reagents of type I and II in the form of solvates, which is sometimes observed in the case of other reagents and, moreover, predominantly in an acid medium [4]. Considering the high pH value, it seems more probable that the other two bidentate reagents involved occupy a corresponding number of coordination positions in a mixed chelate complex and the excess is present in the aqueous phase in the form of anions. Nonetheless, since these additional reagents are colorless or weakly colored (III-V and XII) and may form weakly colored incomplete and mixed chelates, there is the possibility of the formation of extractable compounds with solvated neutral molecules of these reagents, especially in the case of trivalent cations. The latter hypothesis may apply especially to extraction at lower pH values.

Among the reasons for the observed cases of selective extraction with the participation of three chelate formers, some part may be played by the increase in the individuality of the particles during step-wise chelate formation of tri- and tetravalent cations.

This increase in the individuality of incomplete chelate particles may be followed, for example, in the case of acetylacetone [5], 1-nitroso-2-naphthol [6], 2-nitroso-1-naphthol [6], and 8-hydroxyquinoline-5-sulfonic acid [7], where, as a rule, the difference between the logarithms of the second formation constants of chelates of tri- and tetravalent metals is always greater than the corresponding difference for the first formation constants. It may be assumed that the addition to a tri- or tetravalent metal ion of one chelate former residue leads to changes in the steric distribution of electron densities and the appearance of steric hindrance to the addition of new particles or an attack on the central ion by any particles so that the complex particles formed behave more individually than the original ions. In accordance with this, it seems probable that when a particle of another reagent is added to an incomplete chelate complex, the individuality of the particle formed may increase. A further modification of the nature of the particles by the addition of a new chelate former may also lead to an increase in selectivity.

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NEW REARRANGEMENT OF HYDRAZINE DERIVATIVES. PREPARATION OF β-DIALKYLAMINOPROPIONITRILES FROM UNSYMMETRICAL DIALKYLHYDRAZINES AND ACROLEIN

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In an attempt to synthesize previously unknown unsaturated hydrazones by condensation of unsymmetrical dialkylhydrazines with acrolein, we observed a new type of rearrangement with the formation of β-dialkylaminopropionitriles according to the scheme:

$$R_2N-NH_2 + CH_2=CH-CHO \rightarrow H_2O + R_2NCH_2-CH_2-C\equiv N.$$

The reaction was carried out with dimethylhydrazine (R = CH_3, 68% yield of β-dimethylaminopropionitrile) and with diethylhydrazine (R = C_2H_5, 56% yield). The new rearrangement is characterized by rupture of the nitrogen–nitrogen bond under very mild conditions, namely, merely mixing of the reagents in the cold in a weakly acid medium (addition of acrolein to aqueous solutions of hydrazine salts*).

Rearrangements with rupture of nitrogen–nitrogen bonds and the formation of new nitrogen–carbon bonds, which include the reaction we discovered, have been observed up to now only in the aromatic series (benzidine and semidine rearrangements, conversion of diazoamino compounds into aminoazo compounds, conversions of nitrosamines and nitroamines into C-nitroso and C-nitro compounds, etc.).

The reaction with acrolein apparently proceeds through the formation of unsaturated hydrazones $CH_2=CH-CH=N-NR_2$, which immediately rearrange to aminonitriles in a weakly acid medium. The only known case of the formation of nitriles from hydrazine derivatives is the catalytic decomposition of aldehyde phenylhydrazones discovered by A. E. Arbuzov [1], which gives nitriles and aniline and which occurs at temperatures of about 200° in the presence of cuprous chloride, i. e., under much more drastic conditions.

The β-dialkylaminopropionitriles formed from dialkylhydrazines and acrolein in our case have previously been synthesized by cyanoethylation of secondary amines and are interesting as starting materials for the formation of physiologically active preparations and detergents. For more reliable identification of the products of the reaction described, we synthesized β-dimethylaminopropionitrile, β-diethylaminopropionitrile, and a series of their derivatives from acrylonitrile [2, 3].

* A water-soluble, high-molecular substance, which has not yet been examined more closely, was formed in an alkaline medium (addition of acrolein to free dimethylhydrazine). When the reagents were mixed in the reverse order (addition of dimethylhydrazine to acrolein) there was a strong explosion, probably due to spontaneous polymerization of acrolein.

Experimental

Reaction of acrolein and unsymm. dimethylhydrazine. To a cooled solution of 156 g (1 mole) of $(CH_3)_2NNH_2$ (chemically pure) in 300 ml of distilled water was added 60 g (1 mole) of $(CH_3)_2NNH_2$ (b. p. 62.4-64.0° at 765 mm; d^{20}_4 0.7911; n^{20}_D 1.4088). Over a period of 25 min with cooling in ice and continuous shaking, 56 g of freshly distilled, pure acrolein, stabilized with hydroquinone, was added dropwise to the suspension of fine salt crystals obtained. Over a period of 20 min, 120 g of solid potassium hydroxide was added to the reaction mixture. The orange organic layer which separated (90 g after drying with solid potassium carbonate and alkali) was vacuum distilled on a Vigreux column with an efficiency of 12 theoretical plates.

The main fraction with b. p. 71.8-72.0° at 20 mm Hg (171-171.5° at 758 mm) was pure β-dimethylaminopropionitrile; the yield was 67 g (68% of theoretical).

	Found %:	C 60.98;	61.11;	H 10.30;	10.46;	N 28.70;	28.29
$C_5H_{10}N_2$.	Calculated %:	C 61.19;		H 10.27;		N 28.54	

The molecular weight (cryoscopically in benzene) was 97.5, 98.3; calculated for $C_5H_{10}N_2$, 98.15. The equivalent weight (by titration with 0.1 HCl to bromophenol blue) was 98.25. Calculated for $C_5H_{10}N_2$ 98.15 d^{20}_4 0.8698; n^{20}_D 1.4269. n^{20}_C 1.4242; Δ_{FC} 86.0; ω_{FCD} 20.17. MR_D found 28.98; calculated 28.88 (according to Vogel).

An authentic preparation of β-dimethylaminopropionitrile, obtained from dimethylamine and acrylonitrile [3], had b. p. 71.8° at 20 mm; d^{20}_4 0.8704; n^{20}_D 1.4264; n^{20}_C 1.4240; Δ_{FC} 85.2.

Literature data: b. p. 68° at 18 mm [10], 171° at 750 mm [3]; d^{20}_4 0.8705 [3]; n^{20}_D 1.4283 [3].

The melting points of picrates, hydrochlorides, and methiodides of β-dimethylaminopropionitrile samples synthesized from acrolein and from acrylonitrile practically coincided (see Table 1) and mixtures of them did not show depression of melting point.

Hydrolysis of 2.5 g of the substance by boiling with 6.3 g of conc. HCl for 14 hr yielded 1.2 g (98%) of ammonium chloride and 3.7 g of N, N-dimethyl-β-alanine hydrochloride, which had m. p. 180-181° after recrystallization from alcohol. Literature data: m. p. 180.5–182.5° [4]; 191–192° [5].

The equivalent weight (by titration of an alcohol solution with 0.1 N alcoholic KOH to phenolphthalein) was 80.0; calculated for $(CH_3)_2NCH_2CH_2COOH \cdot HCl$ 78.65.

An authentic preparation of dimethyl-β-alanine hydrochloride, obtained analogously from acrylonitrile, had m. p. 180-181° and did not depress the melting point of the product obtained from dimethylhydrazine.

Reaction of acrolein with unsymm. diethylhydrazine. By the method described above, from 45 g (0.5 mole) of 98% diethylhydrazine [6], 78 g of $NaH_2PO_4 \cdot 2H_2O$ in 300 ml of water, and 28 g (0.5 mole) of acrolein we obtained 34.8 g (56%) of β-diethylaminopropionitrile with b. p. 74.5-75.2° at 9 mm.

	Found %:	C 66.49;	66.55;	H 11.16;	11.21;	N 21.90;	21.97
$C_7H_{14}N_2$.	Calculated %:	C 66.62;		H 11.18;		N 22.20	

The equivalent weight (by titration with 0.1 N HCl) was 126.6, 126.4; calculated 126.2; d^{20}_4 0.8650; n^{20}_D 1.4359; n^{20}_C 1.4335; Δ_{FC} 86.1; ω_{FCD} 19.75. MR_D found 38.14; calculated 38.18.

An authentic preparation of β-diethylaminopropionitrile, which we obtained by the action of acrylonitrile on diethylamine [3], had b. p. 75.2° at 9 mm; d^{20}_4 0.8649; n^{20}_D 1.4355; n^{20}_C 1.4331; Δ_{FC} 85.0.

Literature data: b. p. 76° at 9 mm [3], 76° at 11 mm [9], 83.5-84.5° at 13 mm [7], 196° at 735 mm [8]; d^{20}_4 0.8761 [3, 7], 0.8659 [9]; n^{20}_D 1.4380 [3], 1.4343 [7], 1.4356 [8], 1.4354 [9].

Derivatives of the product from the condensation of acrolein with diethylhydrazine were identical with analogous derivatives of β-diethylaminoacrylonitrile (see Table 1) and mixtures of them did not show depression of melting point.

Hydrolysis of 6.3 g of the substance by boiling for 12 hr with 11.5 g of conc. HCl yielded 1.78 g of ammonium chloride* and 9.43 g of amino acid hydrochloride. After recrystallization from alcohol, the hydrochloride had

* Identified by qualitative reactions and determination of chloride ion.

m. p. 135-138° and did not depress the melting point of N, N-diethyl-β-alanine hydrochloride (m. p. 137-139°), synthesized from acrylonitrile through β-diethylaminopropionitrile.

The equivalent weight (by titration with alcoholic potassium hydroxide) was 91.2; calculated for $(C_2H_5)_2NCH_2CH_2COOH \cdot HCl$ 90.75.

Literature data for N, N-diethyl-β-alanine hydrochloride: m. p. 136-138° [5].

TABLE 1

Melting Points of Derivatives of β-Dimethylamino-and β-Diethylaminopropionitriles*

Derivatives	Prep. obtained from react. prod. of acrolein and dialkylhydrazine	Authentic preparation (from acrylonitrile)	Literature data
Derivative of β-dimethylaminopropionitrile			
Picrate	150—151°	150—151°	151°[2,3]
Hydrochloride	197—198°	201—202°	199°[2,3]
Methiodide	153°	153—154°	152°[3]
Derivative of β-diethylaminopropionitrile			
Picrate	84—85°	83—84°	85°[3,8]
Hydrochloride	119—121°	122—123°	120°[3]
Methiodide	155—156°	155—156°	152°[3]

* See [3] for procedures for preparing derivatives.

Infrared spectra of the products from the condensation of acrolein with dialkylhydrazines confirmed that they were identical with authentic preparations of the corresponding dialkylaminopropionitriles. The spectra were plotted on a UR-10 automatic double-beam infrared spectrophotometer (Zeiss, Jena) in the region from 4000 to 650 cm^{-1} with a layer thickness of 25μ*. The spectra contained strong absorption bands at 2247 cm^{-1}, characteristic of nitrile groups, while the characteristic frequencies of C = C, C = O, and C = N double bonds were absent. The very abundant bands in the "fingerprint region" differed sharply for the dimethyl and diethyl derivatives, while those of the authentic β-dialkylaminopropionitriles were completely identical with those of the corresponding products of the rearrangement studied.

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** Original Russian pagination. See C. B. translation.

POLYMERIZATION OF ACETONE

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The conversion of a liquid monomer to a polymer is accompanied by a decrease in the entropy of the system. Therefore, from the most general thermodynamic considerations it follows that in a homogeneous liquid phase, polymerization may proceed only with a positive thermal effect (Q). In actual fact,

$$\Delta Z = \Delta H - T\Delta S,$$

where ΔZ is the change in the isobaric isothermal potential with a change from monomer to polymer, $\Delta H = -Q$ is the change in the heat content, ΔS is the change in the entropy of the system, and T is the absolute temperature. For the spontaneous occurrence of the process, the following inequality is necessary: $\Delta Z < 0$ which, when $\Delta S < 0$, is possible if $\Delta H < 0$ and $[\Delta H] > [T\Delta S]$, i. e., $Q > 0$. The thermal effect of the reaction may be determined as the algebraic sum of the energies of the bonds broken as a result of the reaction and the bonds created, where the former have a negative sign and the latter a positive sign.

If we estimate the thermal effect of the polymerization of carbonyl compounds, for example, acetaldehyde or acetone, then, assuming that the energy of the C–O bond in the polymer is the mean energy of the C–O bond in ethers, we find that the thermal effect of the polymerization of acetone = -6 kcal/mole and of acetaldehyde, 0 (the energy of the C = O bond in acetone equals 156 kcal/mole and in acetaldehyde, 150 kcal/mole, while the mean energy of the C–O bond in ethers equals 75 kcal/mole). Thus, from this approximate evaluation we may draw the conclusion that the polymerization of acetaldehyde and acetone in a homogeneous liquid phase is impossible. However, if in the initial state, the monomeric liquid is changed to a system of ordered monomer molecules, i. e., the entropy of the initial system is decreased, then the picture may be changed substantially. One method of ordering the molecules of a monomer is to freeze the latter. The change from liquid to crystalline monomer is accompanied by a decrease in the entropy of the system by the entropy of fusion. For organic liquids, the entropy of fusion usually lies within the range of 13 ± 3 cal/°C · mole [1], which is obviously commensurate with the change in entropy during the conversion of liquid monomer to an amorphous polymer. The decrease in entropy of the initial system leads to a decrease in the negative value of the polymerization entropy. At sufficient low temperatures, the latter may even change signs. In the latter case, polymerization accompanied by a negative thermal effect seems possible. Thus, in some cases the phase state of the monomer in the system should have a decisive effect on the capacity of this monomer to polymerize, which is determined by the thermodynamic parameters of the initial and final systems. For example, it is well known that acetaldehyde, which is unable to polymerize at normal pressures in the liquid phase, readily polymerizes in the solid state close to the melting point [2-4].

On the basis of these considerations, we attempted to polymerize acetone through the C = O double bond by using the method we developed for low-temperature polymerization in systems obtained by cocondensation of molecular beams of monomer and initiator on a strongly cooled wall [5-7].

The experiments were carried out in an apparatus and by a procedure analogous to those described in [5, 6]. Metallic magnesium was used as the initiator and its vapor was slowly condensed in vacuum together with vapor

of carefully dried acetone on a surface cooled with liquid nitrogen. The ratio of acetone to magnesium in the condensation was approximately 200 : 1. A condensed layer of a vitreous molecular mixture of acetone and magnesium was thus deposited on the cooled wall. As the layer became thicker, the distance between its outer, continuously renewed surface and the cooled wall increased. Due to this, the temperature of the outer surface of the vitrified condensate continuously increased and finally reached a value at which a spontaneous process of coordinated rearrangements of monomer molecules began in the surface layer. In the absence of initiation centers, this process should lead to crystallization of the monomeric glass. However, in the given case the lability of the particles arising in the disorder–order phase transition resulted in their instantaneous polymerization. The same phenomenon could be observed with a gradual increase in the temperature of the wall on which the condensation was carried out. In other words, at the moment that the phase transition occurred, conditions were created in the solid phase which were kinetically favorable to combination of the ordered monomer molecules into polymeric chains*. This resulted in the formation of an acetone polymer, which was a white, elastic mass. The polymer was soluble in the monomer. The polyacetone was very unstable at room temperature and decomposed to form acetone. When a sample of polyacetone was rubbed in the hands, it rapidly changed into drops of monomer. In the absence of oxygen and moisture, the most stable samples of polymer existed for not more than 10-12 hr. A polymer obtained by condensation of acetone together with traces of vinyl acetate was found to be somewhat more stable. A way of stabilizing polyacetone would evidently be blocking of the active ends of the polymeric chains.

The apparatus for condensation of molecular beams was connected to a viscometer. The construction of the apparatus made it possible to prepare solutions of the polymer obtained and measure the viscosity of these solutions directly in vacuum without the admission of atmospheric moisture and oxygen. The specific viscosity of a solution of polyacetone in acetone measured by this method in one experiment was found to equal 0.6 (at a solution concentration of 0.5 g/100 ml).

Work on the example of acetone showed that by using the principle of preliminary ordering of monomeric molecules in the reaction system, it is possible to polymerize substances which are incapable of polymerization under normal conditions. In the given case, this ordering was achieved by crystallization of the monomer. Conditions that are kinetically favorable to the formation of polymeric chains from ordered monomer molecules arise during a phase transition of the disorder–order type in vitrified monomer.

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* The mechanism of polymeric chain formation in an ordered system of monomeric molecules was recently considered qualitatively by Semenov [8].

PROTOTROPIC REARRANGEMENT IN THE DIPYRRYLMETHENE SERIES

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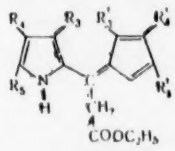
Dipyrrylmethenes with a substituent in the meso position are capable of isomeric conversions, which result in the existence of differently colored forms. To explain this fact, Treibs recently put forward the hypothesis that there exist two forms of dipyrrylmethenes: methene and ethylene forms [1].

To explain the nature of isomeric conversions of this type, we studied a series of dipyrrylmethenes substituted in the meso position with a carbethoxymethyl group.



(I) $R_4 = R_5 = R'_3 = R'_5 = CH_3$; $R_3 = R'_4 = COOC_2H_5$.
(II) $R_3 = R_5 = R'_4 = R'_5 = CH_3$; $R_4 = R'_3 = COOC_2H_5$.
(III) $R_3 = R_5 = R'_3 = R'_5 = CH_3$; $R_4 = R'_4 = COOC_2H_5$.
(IV) $R_4 = R_5 = R'_4 = R'_5 = CH_3$; $R_3 = R'_3 = COOC_2H_5$.

For this purpose we examined the electronic spectra of these compounds, which are very closely connected with the color of the substances.

Compound I, which was obtained by condensation of ethyl 2,3-dimethylcarbethoxypyrryl-5-β-ketopropionate with 2,4-dimethyl-3-carbethoxypyrrole as the base (m. p. 147-148°), had a violet color and its electronic spectrum contained several long-wave maxima (>400 mμ): 505, 584, and 685 mμ (Fig. 1, 1). Compound II, which was obtained by condensation of ethyl 2,4-dimethyl-3-carbethoxypyrryl-5-β-ketopropionate with 2,3-dimethyl-4-carbethoxypyrrole, was isolated as the base and was also in an intensely violet form with a red tint (m. p. 118-120°) and its spectrum had a long-wave maximum at 592 mμ (Fig. 1, 2). When alcohol solutions of I and II were made more alkaline, the long-wave maxima disappeared, curves 3 and 4 (Fig. 1), which almost coincide, were obtained, and the solution became yellow. The bases isolated from the alkaline medium retained the light yellow color, had the following melting points: "yellow form I" 184-185.5° and "yellow form II" 192-193.5°, and a mixed melting point was not depressed (190-193°). The infrared absorption spectra of these substances, which are given in Table 1, were identical. This indicated that "yellow form I" and "yellow form II" were the same compound and the small difference in melting point may have been caused by rotation isomerism.

When solutions of yellow forms I and II were acidified, they again became intensely colored (Fig. 1, 5 and 6), but there was not complete regeneration of the starting substances present before alkali treatment. This is indicated by the fact that when yellow form II was made alkaline, there appeared a maximum at 505 mμ, which was not shown by the violet form II isolated directly from the reaction mixture. This maximum was shown by violet form I, i.e., acidification of yellow form II yielded a mixture of violet forms I and II.

TABLE 1

Compound	Absorption maxima in infrared spectrum, cm^{-1}
I (violet)	3200 2990 2935 2875 1710 1510 1435 1420 1370 1250 1175 1150 1090 1035 1015 980 915 787
II (violet)	3305 2922 2940 2885 1710 1625 1510 1435 1420 1365 1255 1155 1090 1035 992 950 787
I (yellow)	3275 2990 2935 2880 1712 1680 1590 1515 1425 1380 1330 1275 1180 1145 1100 1050 1038 990 965 948 915
II (yellow)	855 798 758

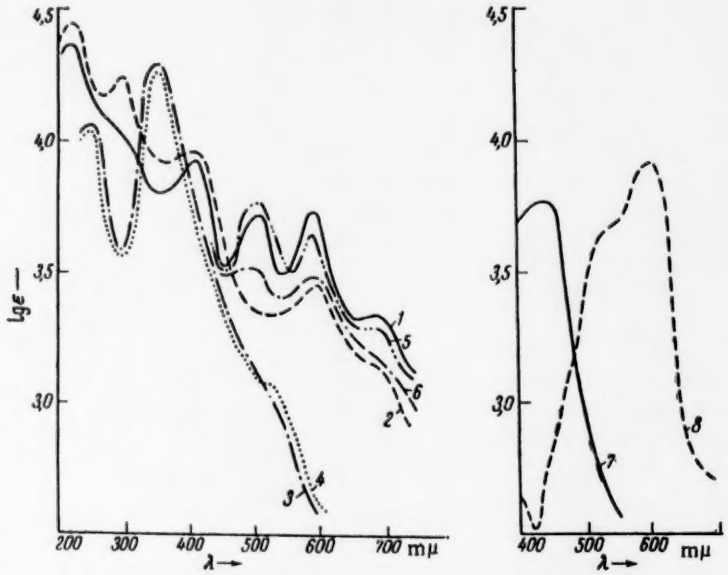
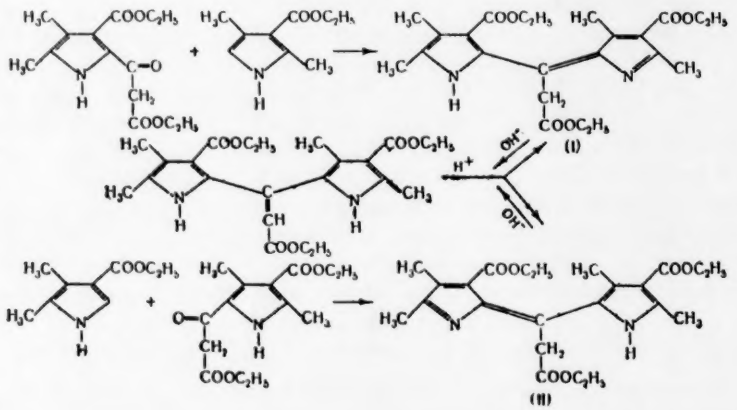


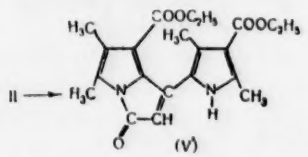
Fig. 1. Absorption spectra (in C_2H_5OH): 1) I, 2) II, 3) I (NaOH), 4) II (NaOH), 5) I (HCl), 6) II (HCl), 7) V, 8) V (HCl).

The interconversions of I and II may be explained by prototropic rearrangements under the influence of the pH of the medium, which lead to one or other of the two intensely colored methene forms or to the yellow ethylene form.



The effect of the electronegative substituents and their position in the rings on the structure of the compounds obtained show clearly in these substituted dipyrrylmethenes. Violet form I is more stable. The isolation

of violet form II involved considerable difficulties due to its great tendency to change into the yellow ethylene form with a change in pH. In addition, compound II showed a tendency to lose alcohol with the formation of a lactam, which could be formed even during the synthesis of II.



(V)

The bright yellow lactam V (m. p. 135-137°), whose spectrum did not contain long-wave maxima (Fig. 1, 7), evidently existed in the ethylene form and when the solution was acidified with conc. hydrochloric acid, this compound changed into a violet form with a reddish tint, which had a long-wave maximum at 595 mμ (Fig. 1, 8), and the absorption in the region of 400 mμ fell strongly.

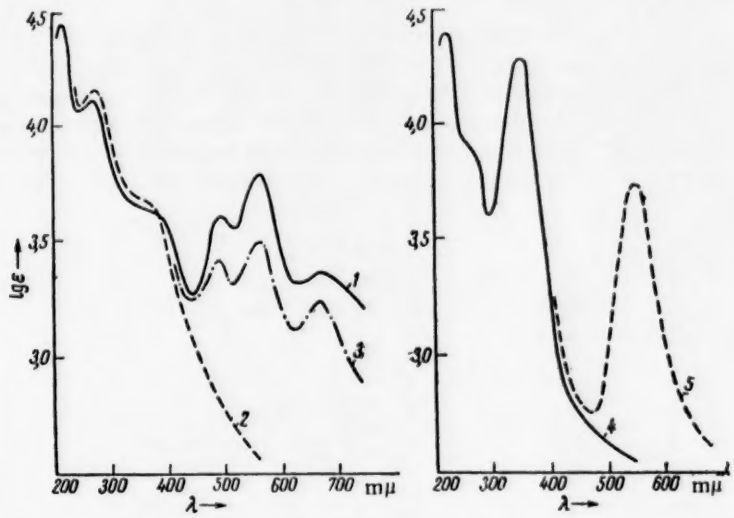


Fig. 2. Absorption spectra (in C_2H_5OH): 1) III, 2) III (NaOH), 3) III (HCl), 4) IV, 5) IV (HCl).

It may be considered that the lower stability of II is connected with the presence of a carbethoxyl group in position 3'. This is confirmed by the following examples. Compound III, which has the carbethoxyl substituents in positions 4 and 4', was isolated as the base in the form of an intensely colored compound (m. p. 167-169°). Its electronic absorption spectrum (Fig. 2, 1) had a series of long-wave maxima at 495, 565, and 670 mμ. When the solution was made alkaline, the violet color changed to light yellow and the long-wave maxima disappeared from the absorption spectrum, while the ultraviolet part was almost unchanged (Fig. 2, 2), i.e., there was a change to the ethylene form. However, an attempt to isolate the yellow ethylene form was unsuccessful due to the reverse change of the substance into the methylene form, which was also formed on acidification (Fig. 2, 3).

Compound IV, in which the carbethoxyl substituents are in positions 3 and 3', behaved oppositely. In contrast to the previous one, this compound was light yellow in the free state (m.p. 159-160°) and long-wave maxima were completely absent from its spectrum (Fig. 2, 4). In the presence of a considerable concentration of hydrochloric acid (up to 5 N), this compound acquired a violet color and a long-wave maximum at 545 mμ appeared in its spectrum (Fig. 2, 5), indicating the formation of the methene form. It was not possible to isolate IV in the methene form because the reverse change to the yellow form occurred as the solution was neutralized. Thus, we may draw the general conclusion that the presence of electronegative groups in positions 3 and 3' promotes the formation of the ethylene form and hampers the formation of the methene form, which exists only in salts in this case [2]. The presence of electronegative substituents in positions 4 and 4' promotes the formation of the methene form.

Compounds I and II, which have carbethoxyl substituents both in positions 3 and 4' and 4 and 3', may be isolated both in the methene and ethylene forms. The presence of an electronegative substituent in position 3' has a greater effect on the tendency of the compound to exist in the ethylene form than the substituent in position 3.

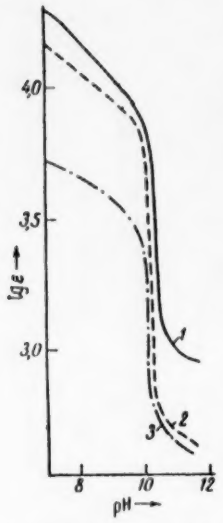


Fig. 3. Curves of titration with 0.01 N NaOH. 1) III, 2) I, 3) II.

The interconversions of methene and ethylene forms examined occur at definite hydrogen ion concentrations. Figure 3 shows curves for the titration of the compounds examined with 0.01 N sodium hydroxide solution. The intensity at the absorption maxima of the corresponding methene forms was used as the indicator. The halt in the change in log ϵ with a continuing change in pH (inflection point on the titration curves) indicates complete conversion to the ethylene form, which does not have long-wave maxima. The reverse change into the methene form was effected most readily in the case of compound III, which does not have a free ethylene form, and with greatest difficulty in the case of IV, where large amounts of concentrated hydrochloric acid were required. The behavior of compounds I and II lay between these extremes in accordance with the fact that they could be isolated both in the methene and ethylene forms.

The investigation of the conversions of substituted dipyrrylmethenes in solutions with different pH values and the study of the electronic and infrared spectra and other properties of these substances showed that the compounds investigated thereupon undergo rearrangements. The different forms of the substances existing at different pH values are structural isomers, differing in the position of the double bonds. The change from one form to another proceeds through a type of prototropic rearrangement.

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CRYSTALLOCHEMICAL DATA ON THE STEREOCHEMISTRY OF COMPLEX COMPOUNDS OF SOME DIVALENT TRANSITION METALS (Fe, Co, Ni, Cu, Pd, and Pt)

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In recent years in the crystallochemistry laboratories of the Institute of General and Inorganic Chemistry and Moscow State University there have been more than 30 x-ray structural investigations of complex compounds of divalent Co, Ni, Pd, and Pt. Together with other data, these results [1-22] make it possible to establish some of the characteristics of the stereochemistry of complex compounds of metals in the horizontal row Fe, Co, Ni, and Cu and the vertical row Ni, Pd, and Pt*.

Table 1 gives statistical data on the coordination polyhedra of Fe, Co, Ni, Cu, Pd, and Pt atoms according to available structural data (we considered only complex compounds, including hexammines and hexahydrates, dimeric complexes, chain structures of the type MA_2X_2, and internal complex compounds; compounds like double oxides and sulfides and other oxygen compounds were not considered). Table 2 gives a general idea of the change in coordination and magnetic state with a change in addends in the series CN, NO_2, NCS, Br, Cl, O, and F, corresponding to a gradual increase in the polarity of the bonds, and with replacement of an acid addend by a neutral substituent.

TABLE 1

Statistical Data on the Coordination Polyhedra in Complex Compounds of Divalent Fe, Co, Ni, Cu, Pd, and Pt

Coordination polyhedra	Fe	Co	Ni	Cu	Pd	Pt
Square		1	19	6	19	29
Tetrahedron		11	1	1		
Octahedron	34	30	51	9		
Elongated square bipyramid				22	?	?
Flattened square bipyramid				3		
Square pyramid				2		
Total number of structures studied	34	42	71	43	19	29

*The divalent state is not characteristic of other elements of Group VIII, i.e., Rh, Ir, and Os, while in the case of Ru, only the two following structures have been investigated: $K_4[Ru(CN)_6] \cdot 3H_2O$, which is isomorphous with the analogous ferrocyanide [23], and $M^{I}Ru^{II}Fe^{III}(CN)_6$, where M^{I} is an alkali metal [24].

In analyzing the structural data, we naturally considered other physicochemical properties (chemical, magnetic, dielectric, and spectral), which are essential in establishing analogies in the structure of separate classes of compounds.

1. As is well-known, compounds of divalent Pd and Pt are invariably diamagnetic and form complexes of planar structure, regardless of their composition. Structural investigations showed that square coordination is retained in complete "purity" and in the crystalline state. The only exceptions are M(diarsine)$_2$I$_2$, (M = Ni, Pd, Pt)[25] [Pt(NH$_3$)$_4$ (NCCH$_3$)$_2$] Cl$_2$ · H$_2$O[26], $M^{II}(NH_3)_2 H_2 \cdot M^{IV} (NH_3)_2 H_4$ (M = Pd, Pt; H = Cl, Br)[27,28] in which the squares of MAs$_4$, Pt(NH$_3$)$_4$, and M(NH$_3$)$_2$H$_2$ are made up to distorted octahedra by pairs of addends, lying at large distances from M (3-3.5 A). However, treatment of these complexes in the form M(ad')$_4$(ad'')$_2$ on the basis of dsp^{3}d (or otherwise dsp^2 + $p_z d_{z^2}$) hybridization of covalent bonds [25] seems very debatable. It seems more probable that there is only an electrostatic interaction between M and the two remote addends ad" This is confirmed by the fact that the distances between ad" and ad' correspond to the sums of the ionic or intermolecular radii.

2. In contrast to Pt and Pd, nickel gives diamagnetic complex compounds with a square configuration only with addends which form the most covalent bonds: in the acido series – only with CN groups,and among normal complex compounds with the composition NiA$_2$X$_2$ - only with some phosphines. Planar coordination is much more common among internal complex compounds. In almost all cases the units of NiN$_4$, NiS$_4$, and NiN$_2$S$_2$ and in many cases, those of NiN$_2$O$_2$ and NiS$_2$O$_2$ have this structure [29]. The latter, like Ni(PR$_3$)$_2$X$_2$, lie at the boundary between diamagnetic and paramagnetic complexes; here the structure depends on relatively second-order factors (on which groups contain the N, S, or P atoms).

As a rule, the other complex compounds of Ni are paramagnetic and have octahedral coordination. The only exception is Ni[P(C$_6$H$_5$)$_3$]$_2$Cl$_2$ (and possibly [(C$_6$H$_5$)$_3$CH$_3$As]$_2$ · NiCl$_4$), to which the authors of [30, 31] assigned a tetrahedral structure. The latter may be explained by the fact that the presence of such large addends as P(C$_6$H$_5$)$_3$ or (C$_6$H$_5$)$_3$CH$_3$As$^+$ cations creates steric hindrance to the formation of polymeric chains or frameworks, which are formed by other halogen-containing compounds of nickel (for example CsNiCl$_3$ and NiA$_2$Cl$_2$, where A = = H$_2$O or Py [32, 13]). On the whole, tetrahedral coordination is not characteristic of normal complex compounds of Ni (see [33] for more details).

TABLE 2

Relation of Coordination of Metal Atom to Complex Composition

Element	$[MeX_n]^{-m}$								MeA_2X_2	MeA_4X_2	MeA_4X_2
	CN	NO_2	NCS	Br	Cl	F	O	spinels			
Fe	Octahedron (low-spin)		Octahedron (high-spin)					Tetrahedron with all M^{III} except Fe^{III}	Octa-hedron	Octa-hedron	Octa-hedron
Co	Octahedron (low-spin)		Tetrahedron (high-spin)			Octa-hedron (high-spin)		Octahed. w. Fe^{III}, tetrahed. w. Cr^{III}, Mn^{III}, Co^{III}	Tetrahed. octahed. (two isomers)	Octa-hedron	Octa-hedron
Ni	Sq. (low-spin)		Octahedron (high-spin)*					Octahed. w. all M^{III} except Cr^{III}	Square, octa-hedron**	Octa-hedron	Octa-hedron
Cu	Octahedron		Flattened tetrahedron					Dist. octahed. w. all M^{III}, exc. Cr^{III} and Mn^{III}	Square, dist. octa-hedron, pyramid	Square, distorted octa-hedron	Distorted octa-hedron
	Distorted octahedron										
Pd, Pt	Square (low-spin)							—	Square	Square	—

* With the possible exception of [As(C$_6$H$_5$)$_3$CH$_3$]$_2$NiCl$_4$.

** With the exception of Ni[P(C$_6$H$_5$)$_3$]$_2$Cl$_2$ (tetrahedron).

3. The stereochemistry of compounds of Co^{II} differs substantially from that of Ni^{II}. In the series of acido complexes, the change from low-spin to high-spin compounds occurs later – after NO_2 groups and low-spin compounds are characterized not by planar, but by octahedral coordination of M, while high-spin compounds (in the case of NCS, Br, and Cl) are not octahedral, but tetrahedral. It is only with a change to the most electronegative addends, namely, F and O, that the coordination of Co^{II} and Ni^{II} becomes the same - octahedral*. The change from tetrahedral to octahedral complexes is promoted not only by an increase in the polarity of the Co-X bond, but also by replacement of acid addends by such neutral addends as H_2O, NH_3, Py, thio, etc. Thus, compounds with the composition CoA_2X_2 (where X = NCS, Br, and Cl) have two modifications, one of which retains the tetrahedral and the other has octahedral coordination (polymeric chain structure); compounds CoA_4X_2 and more so CoA_6X_2 are always built up from octahedral complexes.

As regards capacity to form tetrahedral complexes, Co occupies a special position among divalent transition metals of Groups VIII and Ib.

4. Structural data on complex compounds of divalent iron are very limited. Available material appears to show that only octahedral coordination is characteristic of Fe^{II} in complex compounds. Consequently, in low-spin compounds, (cyano and nitro), Fe^{II} behaves analogously to Co^{II} and in high-spin compounds, analogously to Ni^{II}*.

5. As regards stereochemistry, divalent copper occupies an intermediate position between Ni^{II} and Pd^{II} and Pt^{II} on the one hand, and between Ni^{II} and Co^{II}, on the other. Like Pd and Pt, copper sometimes gives purely planar complexes and also planar complexes supplemented by an M–M bond. However, coordination in the form of an elongated bipyramid is most characteristic of Cu^{II}. The filling of all five levels of the 3d shell of the Cu^{II} atom by ten electrons makes it possible to compare such complexes of Cu both with spin-paired square complexes of Pt, Pd, and Ni and with spin-free octahedral complexes of Ni. The similarity to planar complexes is emphasized by the fact that the Cu–ad' distances (to the four addends lying around the square) are close to the M–ad distances (M = Pt, Pd, and Ni) in square complexes and less than Ni-ad in octahedral complexes; the similarity to octahedral complexes lies in the structural similarity of many Cu compounds and paramagnetic Ni compounds (for example, CuF_2 and NiF_2, $CuCl_2$, $CuBr_2$ and $NiCl_2$, $NiBr_2$, $CsCuCl_3$ and $CsNiCl_3$, $K_2Pb[Cu(NO_2)_6]$ and $K_2Pb[Ni(NO_2)_6]$, $Cu(NH_3)_4(NO_2)_2$ and $Ni(NH_3)_4(NO_2)_2$, etc.). In many of the cases listed, the structural pattern of the Cu compound may be represented as a distortion of the structure of the analogous Ni compound. The presence of one vacant space in the d shell of the Cu^{II} atom is associated with the tendency of copper to show distorted or low-symmetry coordinations: unequally elongated octahedron, a tetragonal-pyramidal environment, and a related isomer of a tetragonal-bipyramidal complex – a "flattened" octahedron [34].

On the other hand, in the series of copper halides there is a change from structures characteristic of Ni^{II} to structures characteristic of Co^{II}: $CuCl_2$ and $CsCuCl_3$ are isostructural (with distortion) with the analogous Ni compounds, while Cs_2CuCl_4 is isomorphous with Cs_2CoCl_4. Distorted tetrahedral coordination may be expected in thiocyanate compounds of copper (for example, in $Cu(NCS)_4Hg$, whose composition is analogous to that of the analogous double salt of Co and Hg, but not to that of the double salt of Ni and Hg).

6. Many of the compounds of divalent metals examined are isomorphous. Isostructural formations appear in two groups of compounds: 1) among low-spin compounds of the vertical series Pt, Pd, Ni, where this results from the creation of hybrid covalent bonds on the basis of analogous electronic systems**; 2) among the most ionic high-spin compounds of the horizontal series Fe, Co, and Ni (and Cu with distortion of the coordination polyhedron), where the structure of the crystal is determined by the stabilizing effect of the electrostatic field of the addends, which in all cases (regardless of the number of electrons at the central atom) is more favorable with octahedral coordination than with tetrahedral. In the intermediate region, i.e., with a change from the most electronegative addends F and O to Cl, Br, and NCS, the structure of the complex is determined by the superposition of the two effects. Calculations on oxides and hydrates show that the excess stabilizing force of an octahedral field as compared with a tetrahedral field falls in the series Ni, Cu, Fe, and Co [35, 36] (according to [36], this excess equals

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* The exceptions are oxygen compounds of the spinel type, $M^{II}M_2^{III}O_4$, where Fe^{II} and Co^{II}, much more frequently than Ni^{II} and Cu^{II}, are displaced from the tetrahedral spaces by trivalent metal atoms [35, 36]. Tetrahedral coordination of Co^{II} is also found in $BaCoO_2$ and of Fe^{II}, in some sulfides.

** In individual cases (largely in internal complex compounds with organic addends of sufficiently "rigid" structure), Cu^{II} compounds are also isomorphous with low-spin Ni^{II} compounds, despite the presence of an extra electron at the Cu atom.

22.8, 15.6, 2.9, and 2.1 kcal, respectively). Therefore, Ni^{II} shows least tendency for a change from octahedral coordination to another, while Co^{II} shows the greatest tendency. On the other hand, the actual tendency to form tetrahedral covalent bonds is apparently connected with symmetrical filling of the energy levels of the d shell by electrons which do not participate in bonds. Therefore, such bonds are formed in Co^{II} compounds (configuration $d^7 = d_\gamma^4 d_\epsilon^3$), and much more rarely in Fe^{II} compounds (configuration $d^6 = d_\gamma^3 d_\epsilon^3$ with unsymmetrical filling of the d_γ doublet).

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COPRECIPITATION OF MICROAMOUNTS OF GERMANIUM WITH IRON HYDROXIDE

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In recent years, work has appeared in which the coprecipitation of various metals with insoluble hydroxides is explained by ion-exchange properties of the latter [1]. In most investigations of the adsorption properties of ferric hydroxide, the coprecipitation of various divalent cations with it has been examined. Kurbatov, et al. [2], have given a summary of this work. A much smaller number of communications have been devoted to the coprecipitation of elements which are present in aqueous solution as anions with iron hydroxide. Of these, we should mention the work of Plotnikov [3, 4] on the coprecipitation of selenium and tellurium with $Fe(OH)_3$.

TABLE 1

Effect of Temperature on the Coprecipitation of Germanium

Temp., °C	Ge coprecipitated, %
20	99
40	97
70	100
80	99

Summarizing the results obtained, it may be observed that in the case of an adsorption or ion-exchange mechanism for coprecipitation, complete coprecipitation of metals is attained after a comparatively long time [2] at ratios Me: Fe $\leq$ 1: 1000, while an increase in the concentration of foreign electrolyte reduces the completeness of coprecipitation.

Coprecipitation with ferric hydroxide is often used in the chemical determination of germanium [5]. Thereupon there is not only separation of germanium from the main amount of Cu, Zn, Cr, etc., but also considerable concentration of it in the solutions formed when the hydroxide with the coprecipitated germanium is dissolved in dilute hydrochloric acid. Meanwhile, the literature contains no data on the coprecipitation mechanism and the effect of various factors on the completeness of coprecipitation of microamounts of germanium with iron hydroxide.

In the present communication we present the results of an investigation of the coprecipitation of germanium, present in solution as germanic acid, the anion $HGeO'_3$ and, possibly, $Ge_5O''_{11}$ [6], with ferric hydroxide in relation to temperature, time of contact of the precipitate with the solution, amount of hydroxide introduced, germanium concentration, and solution pH.

Tables 1 and 2 give data on the effect of temperature and the time of contact of the precipitate with the solution on the completeness of germanium coprecipitation (Ge concentration 1 γ/ml, pH 8, Ge: Fe = 1 : 100). The data presented show that the completeness of coprecipitation of germanium was the same over the temperature range from 20 to 80° and, within the limits of experimental error, complete coprecipitation was reached even after the solution had been in contact with the precipitate for two minutes and germanium was not released into the solution again even after prolonged contact of the solution and the precipitate.

A study of the relation of germanium coprecipitation to the Ge: Fe ratio (Fig. 1) showed that even at Ge: Fe ratios of 1: 20 (at a germanium concentration of 1 γ/ml) there was complete coprecipitation of germanium with the hydroxide and a decrease in this ratio did not lead to solution of germanium.

TABLE 2

Effect of Time of Contact of the Precipitate with the Solution on the Completeness of Germanium Coprecipitation

Time of cont. of precip. with solution, min	Ge co-precipitated, %
2	99
5	98
10	102
30	99
60	103
120	101
24 hr	100

The addition of ammonium sulfate to the solution, on the one hand, did not decrease the degree of germanium precipitation at low Ge : Fe ratios and, on the other, increased the degree of germanium precipitation at high ratios, probably due to better coagulation under these conditions.

The experimental data presented in Fig. 2 show that practically complete coprecipitation of germanium with the hydroxide may be achieved at germanium concentrations of 0.01 γ/ml at a Ge : Fe ratio of 1 : 1000 in 2% $(NH_4)_2SO_4$ solution and consequently iron hydroxide may be used for the preliminary concentration of germanium (by a factor of ~100) in the analysis of very dilute solutions. With a Ge : Fe ratio of 1 : 100, it is possible that complete coprecipitation begins only with 0.05 γ/ml due to the insufficient degree of coagulation of the hydroxide in such dilute solutions.

The relation of germanium coprecipitation to solution pH is shown in Fig. 3. Complete coprecipitation was attained over the range from pH 6 to 9.5. Figure 3 shows that complete precipitation of iron as hydroxide was reached before there was 100% coprecipitation of germanium on it and at pH > 9.5, part of the germanium remained in solution, while the amount of precipitated hydroxide was unchanged. Thus, the use of coprecipitation with iron hydroxide makes it possible to determine germanium in very dilute solutions (≥ 0.01 γ/ml).

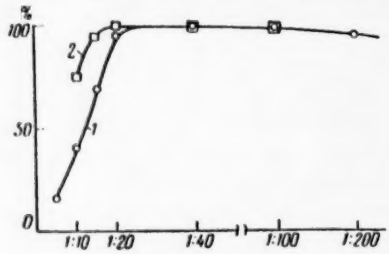

Fig. 1. Relation of Ge coprecipitation to the amount of iron hydroxide. pH 8, t = 70°, Ge conc. 1 γ/ml: 1) without addition of $(NH_4)_2SO_4$; 2) in 2% $(NH_4)_2SO_4$ solution.

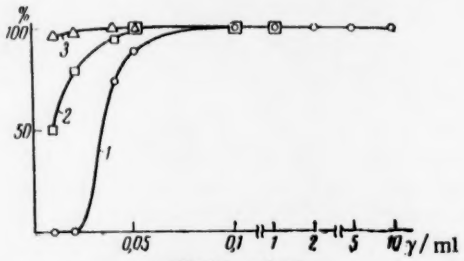

Fig. 2. Effect of the Ge concentration in solution on the completeness of precipitation by iron hydroxide. pH 8, t = 70°; 1) Ge : Fe = 1 : 100, without $(NH_4)_2SO_4$; 2) Ge : Fe = 1 : 100 in 2% $(NH_4)_2SO_4$ solution; 3) Ge : Fe = 1 : 1000, in 2% $(NH_4)_2SO_4$ solution.

The data presented indicate that there is probably coprecipitation of iron germanates, which are insoluble at pH 6-9.5, on iron hydroxide, rather than adsorption of germanic acid on the latter. The following facts also support this: the rapidity of complete coprecipitation, the independence of complete coprecipitation of the concentration of foreign electrolyte, and the fact that complete coprecipitation is attained at comparatively high Ge : Fe ratios.

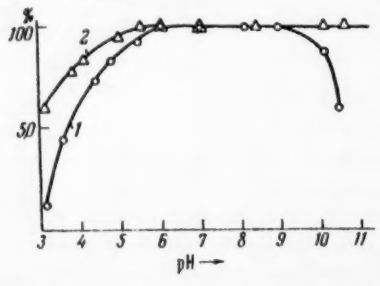

Fig. 3. Relation of germanium (1) and iron hydroxide (2) coprecipitation to the pH of the system. Ge conc. 1 γ/ml; Ge : Fe = 1 : 100, t = 70°, 1) percent Ge precipitation, 2) percent Fe precipitation.

Experimental

Working solutions were prepared from chemically pure grade preparations and distilled water. Germanium was used as a solution of germanium dioxide in dilute hydrochloric acid with pH 5. The iron was added as an aqueous solution of ferric ammonium alum. The hydroxide was precipitated by the dropwise addition of ammonia to the solution prepared.

The amount of germanium coprecipitated with the iron hydroxide was determined in the following way: the hydroxide formed was collected by filtration and dissolved on the filter in a small amount of 4 N hydrochloric acid. The germanium was extracted from an aliquot portion of the solution obtained with carbon tetrachloride by the method of Nazarenko et al. [7] and determined colorimetrically on an FÉKM-57 instrument with a No. 4 light filter (transmission

maximum at 508 mμ). The relative error in the measurements did not exceed ± 5%. An LP-5 potentiometer was used for measuring the pH of the solutions.

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ISOLATION OF WEIGHABLE AMOUNTS OF PURE PROCTACTINIUM-231

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Despite the rapid development of work on the chemistry of protactinium in the last decade in a number of countries, protactinium has remained one of the least studied elements and this is explained by the difficulty of isolating weighable amounts of its long-lived isotope Pa^{231}, which is most suitable for chemical investigations.

The raw materials for protactinium-231 production are various waste products from uranium production, the large supplies of which make it possible to prepare kilogram amounts of the element. However, technological methods described in the literature for processing these wastes are complex and have many stages, including co-precipitation with carrier, extraction, and ion exchange [1-6]. The lack of a single method suitable for various crude sources of the element is connected with the fact that the behavior of protactinium, the concentration of which in uranium wastes is 10^{-6}–10^{-5} weight %, is strongly affected by accompanying elements and the nature of the latter depends on the composition of the original ore and the main technological method.

For the concentration of protactinium from uranium production wastes we made use of its capacity to be sorbed from nitric acid solutions onto manganese dioxide precipitates [7] and this gave a high degree of purification from the main macrocomponents of the starting material, i.e., aluminum, iron, and calcium. In this way we obtained a concentrate with the following composition: MnO_2 81%; SiO_2 4.1%; Fe_2O_3 2.4%; Al_2O_3 0.9%; TiO_2 0.4%; ZrO_2 0.3%; CaO 0.03%; P_2O_5 1.5%; As_2O_5 2.9%. The protactinium content, determined by the method in [8], was $2.5 \cdot 10^{-4}$%, which was 100 times greater than the concentration in the starting material.

When the concentrate was treated with hydrochloric acid, the silicic acid in it was liberated as a gel and the protactinium was distributed between the solution and precipitate. The nature of the distribution depended on the acidity of the solution and the completeness of coagulation of the silicic acid.

The silicic acid gel obtained by solution of the concentrate in 1 N HCl with $NaNO_2$ added contained all the protactinium present in the concentrate. The main impurities in it were Fe, P, As, Mn, Ti, Zr, and Nb.

After removal of the silicic acid by alkali treatment or distillation with hydrofluoric acid and solution of the residue in hydrochloric acid, the protactinium was isolated with a precipitate of zirconium, titanium, and niobium phosphates, the main component of which was zirconium. It should be noted that these elements are chemically related to protactinium and normally accompany it during concentration processes. Their separation is the main difficulty in the production of pure protactinium-231.

The methods of fractional crystallization and fractional precipitation [1, 9], which were examined by a number of investigators for this purpose, require many repetitions of individual operations and are very laborious and of low efficiency. The use of extraction with diisobutylcarbinol, which was recently proposed for the purification of protactinium [10], is limited by the shortage of this extractant.

Work [11-15] has been devoted to the separation of protactinium from other elements by anion exchange in concentrated HCl solutions or in mixtures of HCl and HF. These investigations were concerned with the separation of microamounts of protactinium, niobium, zirconium, and titanium or the separation of no more than 1-2 mg amounts. We developed a method of freeing milligram amounts of protactinium from amounts of niobium, titanium, and zirconium exceeding the protactinium content by factors of tens and hundreds.

TABLE 1

pH Dependence of the Distribution Coefficients of Protactinium and Niobium between MnO_2 and 0.5 N NH_4F Solution

pH	$K_{p(Pa)}$	$K_{p(Nb)}$	Ratio: $K_{p(Nb)} : K_{p(Pa)}$
5,48	19,8	560,0	28,3
5,23	16,0	380,4	24,0
4,97	11,0	232,0	21,4
4,65	6,1	110,0	18,0
3,90	5,1	26,7	6,3
2,91	4,3	17,1	4,6
1,62	3,7	14,8	4,0
1,00	3,4	14,6	4,3
0,50	3,5	13,3	3,8

Footnote: The pH was measured on a P-4 potentiometer with quinhydrone and calomel electrodes.

A study of the possibility of separating these elements on home-produced anionites of the grades AV-16, AV-17, and AN-2F under the conditions described in the literature as optimal for Dowex-1 resin (7 N HCl used) did not give the desired result. Manganese dioxide was found to be more effective. The sorption of protactinium from 10 N HNO_3 on a column of MnO_2 made it possible to separate it from large amounts of zirconium and titanium, which were held more weakly by this adsorbent and could be removed from the column completely by washing with 10 N nitric acid. The analogous behavior of protactinium and niobium under the given conditions necessitated a special examination of possibilities for separating them. For this purpose we studied the pH dependence of the distribution coefficients (K_p) of protactinium and niobium between manganese dioxide and 0.5 N NH_4F solution, using solutions of protactinium-233 and niobium-95 (Table 1). The distribution coefficients were determined as the ratio of the activities of 1 g of sorbent and 1 ml of solution. The Nb^{95} used in the work was the standard commercial isotope and the Pa^{233} was obtained by neutron irradiation of thorium nitrate and was freed from impurities by the method in [16, 17]. The Pa^{233} isolated was identified and its radiochemical purity checked by determination of the half-life and the maximum energy of the β-radiation. The values found (T = 27.2 days and $E_{\beta max}$ = 0.57 Mev) coincide with literature data [18].

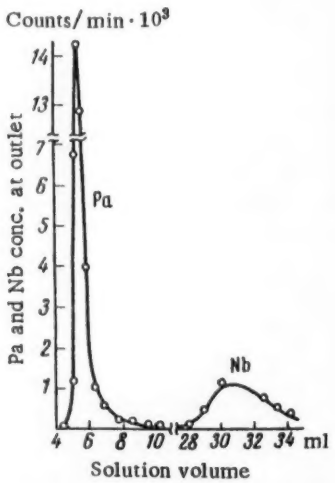

Fig. 1. Elution of protactinium and niobium with a solution of 0.5 N HNO_3 + 0.2 N NH_4F.

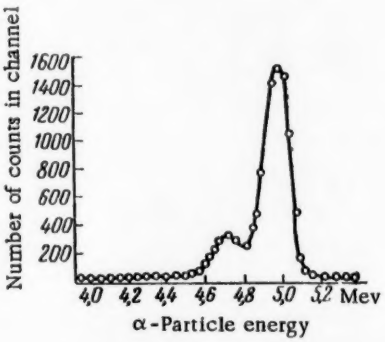

Fig. 2. α-Radiation spectrum of protactinium-231 obtained.

The stronger dependence of K_p on the solution pH for niobium than for protactinium led to an increase in the ratio $K_{p(Nb)} : K_{p(Pa)}$ as the hydrogen ion concentration decreased. However, the high absolute values of the distribution coefficients in the region of pH > 4.5 caused slow elution of protactinium and niobium sorbed on a manganese dioxide column and made it necessary to work in the acid region despite the fact that $K_{p(Nb)} : K_{p(Pa)}$ at low pH values became less favorable.

The use of acid solutions of NH_4F for the elution of protactinium and niobium made it possible to separate these elements completely when they were sorbed on a manganese dioxide column. Figure 1 shows the elution curve for protactinium-233 and niobium-95 with a solution of 0.5 N HNO_3 + 0.2N NH_4F. The column diameter was 0.4 cm, the height of the manganese dioxide layer 30 cm, the grain size 0.17-0.25 mm, and the solution flow rate 0.1 ml · cm^{-2} · min^{-1}. The manganese dioxide for filling the column was prepared by oxidation of $MnSO_4$ with $KMnO_4$ solution in a neutral medium [19]. The precipitate obtained was dried at 110-120° and then sieved to give the required fraction.

The procedure developed for the separation of protactinium from zirconium, titanium, and niobium on model solutions was applied to the concentration of protactinium-231 in the precipitate of zirconium, titanium, and niobium phosphates. This product was boiled with 10% NaOH solution and the hydroxides obtained treated with HNO_3. The nitric acid solution was passed through a column of manganese dioxide and then the titanium and zirconium removed by washing with 10 N nitric acid. The protactinium was separated from the niobium by washing with a solution of 0.5 N HNO_3 + 0.2 N NH_4F.

TABLE 2

Behavior of a Mixture of Pa^{231} and Pa^{233} during Precipitation on Carriers

Carrier	Medium	Degree of co-precipitation in % of original	Ratio of Pa^{233} and Pa^{231} activities		
			original solution	supernatant solution	precipitate
MnO_2	10 N HNO_3	53.1	3.1	–	3.1
Nb_2O_3	6 N HNO_3	66.0	20.3	20.8	–
CaF_2	1 N HNO_3	56.2	3.4	3.2	–
Zr mandelate	6 N HCl	15.0	9.6	–	10.0
Zr phosphate	3 N HCl	91.0	17.7	16.4	–

During the elution of the protactinium, a small amount of manganese (a few μg/ml) passed into the eluate and for the removal of this, the solution was passed through a column of KU-2 resin. The protactinium, which forms a stable, negatively charged complex with fluoride ions, was not absorbed by the resin and passed through with the filtrate; the manganese remained on the column.

As a result of the operations described, milligram amounts of protactinium were obtained from several kilograms of the original concentrate. The chemical purity of the product was established by spectral analysis of a sample containing 1.5 μg of protactinium. The characteristic protactinium lines at 2732.2, 2743.9, and 2755.9 A were observed in the region of 2500-3000 A on a focussing spectrograph. No lines of other elements were detected in this region.

The element isolated was further identified by isotope dilution and from the energy of the α-radiation. In the isotope dilution method, the behavior of the protactinium-231 isolated was compared with that of protactinium-233 during coprecipitation with some carriers. Before precipitation or the introduction of a prepared carrier, the mixture of Pa^{231} and Pa^{233} was heated and kept for 2 days for isotopic equilibrium to be reached. The content of each isotope was determined by measurements on a disk with a portion of solution deposited on it on a type B-2 apparatus with a T-25-BFL end-window counter, which recorded the β-radiation of Pa^{233}, and then on a "Flocks" apparatus, which measured the α-radiation of Pa^{231} directly with a scintillation counter. The results obtained are given in Table 2.

The fact that the ratio of the Pa^{233} and Pa^{231} activities remained constant during distribution between two phases indicated that these isotopes behaved analogously during various coprecipitation processes and consequently were chemically identical.

An investigation of the nature of the radiation of the product isolated* showed (Fig. 2) that its nuclear properties coincided with available literature data for protactinium-231 [18] and established the radiochemical purity of the preparation obtained.

*The radiation of the Pa^{231} sample was investigated by S. A. Baranov and Yu. F. Rodionov in the Nuclear Spectroscopy Laboratory of the I. V. Kurchatov Institute of Atomic Energy, Academy of Sciences, USSR.

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SYNTHESIS OF SILICON DERIVATIVES OF POLYVINYL ALCOHOL

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Polyvinyl alcohol is known to have the structure of a 1,3-glycol with a small number of 1,2-glycol units.

For modifying the properties of polyvinyl alcohol, it seemed interesting to prepare various silicon derivatives of it. There is no information at all in the literature on the preparation of such derivatives.

We attempted to prepare silicon derivatives of polyvinyl alcohol (organosilicic esters) with the general formula:

$$-CH_2-\underset{\underset{OSiR_3}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-$$

where R is alkyl, aryl, or aralkyl.

For the preparation of such derivatives of polyvinyl alcohol we used the following reactions: a) reaction of chlorosilanes with polyvinyl alcohol and its alcoholates in a heterogeneous medium; b) reaction of chlorosilanes with partially hydrolyzed polyvinyl acetate in a homogeneous medium; c) reaction of trialkylaminosilanes with polyvinyl alcohol in pyridine. In carrying out the reaction of chlorosilanes with polyvinyl alcohol, and its alcoholates, we encountered difficulties due to the fact that chlorosilanes react readily with water, pyridine, formamide, and other agents used for the solution (or swelling) of polyvinyl alcohol.

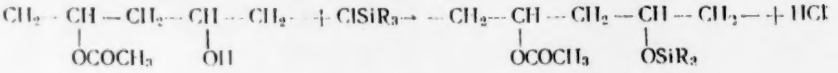
Due to this, an attempt was made to carry out a heterogeneous reaction of anhydrous polyvinyl alcohol, its alcoholate, and alkali derivatives (containing 7-8 mol. % of Na), synthesized by known methods [1], with alkylchlorosilanes in benzene. For the reaction we used polyvinyl alcohol obtained by alkaline methanolysis of polyvinyl acetate (with a viscosity of 20 centipoises and a residual acetyl group content of 1.03 mol. %). The reactions were carried out by stirring a benzene suspension of finely ground powders of polyvinyl alcohol, its alcoholate, and its alkali derivative with trimethylchlorosilane (2-4 moles per polyvinyl alcohol unit) at 20 to 70° for 7-24 hr.

Under heterogeneous conditions it was impossible to effect any appreciable replacement of hydroxyl groups of polyvinyl alcohol by alkylsilyl radicals.

To carry out the reaction under homogeneous conditions, we then used partially hydrolyzed polyvinyl acetates, which retained their solubility in benzene. They were obtained by known methods, namely, catalytic alkaline alcoholysis in absolute methanol [2]. For the products to retain their solubility in benzene, the alcoholysis was continued until there was not more than 10 mol. % of hydroxyl groups in the polyvinyl acetate chain.

The reaction with trialkylchlorosilanes (used in excess) was carried out with a solution of these partially hydrolyzed polyvinyl acetates in benzene or in a mixture of benzene and dioxane (for polyvinyl acetates containing ≅ 10 mol. % of hydroxyl groups). The experiments were carried out in an absolutely anhydrous medium

in a three-necked flask with a reflux condenser with a calcium chloride trap, a stirrer, and a dropping funnel. In this case the reaction proceeded according to the scheme:



Finely powdered magnesium carbonate was suspended in the reaction medium for binding the HCl liberated. The product obtained was precipitated from the filtered solution with ligroin and purified by solution in dioxane and precipitation with water twice.

The results of some experiments are given in Table 1.

TABLE 1.

Expt. No.	Reaction time, hr	Partially hydrolyzed PVA,* g	TMCS, g**	TMCS / partially hydrolyzed PVA	Medium	Reaction temp., °C	Yield of reaction products, g	Si content, mol.%	OH groups replaced, % on silicon
1	7	2	10.8	50 : 1	Benzene	60	1.5	1.32	17.6
2	78	4	21.5	55 : 1	Benzene	20	2.7	4.8	64
3	46	2	12	60 : 1	Benzene	40	1.3	2.3	30.5
4	52	3	18	60 : 1	Benzene in the presence of $MgCO_3$	50	1.63	5	66.7
5	75	3.4	4	4 : 1		20	2.8	3.8	52

*Partially hydrolyzed polyvinyl acetate.

**Trimethylchlorosilane

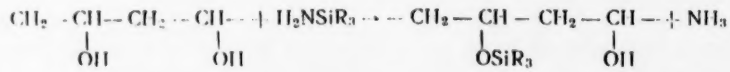
Footnote: The starting partially hydrolyzed PVA had a characteristic viscosity of 0.37 and contained 7.8 mol.% of hydroxyl groups in Experiments 1-4 and 7.3 mol. % in Experiment No. 5.

Thus, under the conditions adopted, 50-70% of all the free hydroxyl groups of the partially hydrolyzed polyvinyl acetate were substituted. The powdered magnesium carbonate which we used to bind the HCl liberated played a very important part and made possible a high degree of substitution of the hydroxyl groups.

No appreciable destruction of the chains was observed as was established by comparison of the characteristic viscosity of the starting partially hydrolyzed polyvinyl acetate in acetone ($[\eta]$ = 0.37) with that of the reaction product containing 4.8 mol. % of silicon ($[\eta]$ = 0.43). The copolymers obtained with a silicon content of 4-5 mol. % had a higher vitrification point (T_V = 38°) than polyvinyl acetate (T_V = 28°). The rise in vitrification point was evidently associated with the presence of hydroxyl groups and the formation of hydrogen bonds between chains.

Work on the preparation of such copolymers is continuing with a smaller proportion of trimethylchlorosilane (right down to the theoretical amount). The reaction with partial acetals of polyvinyl alcohol, which are soluble in benzene and dioxane, is carried out analogously.

Aminosilanes are known to react readily with low-molecular alcohols to form orthosilicic esters [3]. We used an analogous reaction for the preparation of corresponding derivatives of polyvinyl alcohol according to the scheme:



For the reactions we used polyvinyl alcohol with M = 27,000, containing 1.03 % of residual acetyl groups, and triethylaminosilane, obtained by the reaction of triethylchlorosilane with liquid ammonia [4].

The triethylaminosilane had the following characteristics: b.p. 134-139°, Si content 21.99% (calculated, 22.06%), n_D^{20} 1.4259.

The reaction was carried out in the same apparatus as for the reaction of partially hydrolyzed polyvinyl acetate with alkylchlorosilane. Dry pyridine (in which polyvinyl alcohol swells and triethylaminosilane dissolves) was used as the reaction medium and there was complete protection from atmospheric moisture. The polyvinyl alcohol was first allowed to swell in pyridine for 18-20 hr at normal temperature or for 2-3 hr at 100° and the reaction mixture was stirred for a definite time. After approximately 1.5-2 hr, the reaction mixture became completely homogeneous. The reaction product was isolated by precipitation with various organic liquids as the solubility of the product varied considerably, depending on the degree of substitution. Thus, for example, ligroin was used as the precipitant for a polymer containing 15 mol. % of Si. The product isolated was reprecipitated twice, washed, dried in vacuum, and then analyzed for Si content (by combustion in the presence of HNO_3 and H_2SO_4 and firing at 1000°) and free hydroxyl groups (by Verley's method).

TABLE 2

Results of Experiments on the Preparation of Triethylsilyl Ethers of Polyvinyl Alcohol

Experiment No.	PVA*, g	TEAS**, g	PVA/TEAS	Reaction temp., °C	Reaction time, hr: heating	Reaction time, hr: total	Degree of substitution, mol. %	OH content, mol. %
1	2,65	8	1 : 1	80	12,44	44	26,4	
2	5	25	1 : 1,38	100	5	168	13,7	
3	1	6,5	1 : 2	100	4	4	19,6	
4	2,23	4,2	1 : 0,7	80	16	48	17	
5	0,9	4,81	1 : 1,8	100	12	46	36,3	61
6	4	24,15	1 : 2	100	14	192	45	37,2
7	0,9	12,53	1 : 4	100	12	48	44,5	51,4
8	3	19,5	1 : 2	100	22	110	49,7	34,9
9	1	6,3	1 : 2	100	34	168	78	
10	2	13,7	1 : 2	100	53	168	61,6	35,7

* Polyvinyl alcohol

** Triethylaminosilane

Footnote: The total reaction time includes the time that the reaction mixture was kept at normal temperature between heating periods.

It was established that the organosilyl ether of polyvinyl alcohol was formed under the given conditions. Since it was difficult to detect the ammonia liberated during the reaction in pyridine, special experiments were carried out on the reaction of triethylaminosilane with the organosilicic ester of polyvinyl alcohol, which was prepared by the above method, contained 28.7-31 mol. % of Si, and was soluble in dioxane and benzene. The liberation of ammonia and an increase in the degree of substitution of the hydroxyl groups of polyvinyl alcohol were demonstrated qualitatively and quantitatively by the reaction with triethylaminosilane in benzene.

The results of some experiments are given in Table 2. As this table shows, triethylsilyl ethers of polyvinyl alcohol with various degrees of substitution were obtained (up to 78 mol. %).

Data on the solubility of some of the products obtained, which are given in Table 3, show that even with the introduction of 13 mol. % of triethylsilyl groups, the product was insoluble in water, but soluble in some organic solvents. When the content of triethylsilyl groups was 31.6 mol. %, the polymer was completely soluble in benzene and when the content of these groups was 61.6 mol. %, the product was soluble in ligroin. This solubility of triethylsilyl ethers of polyvinyl alcohol, namely, solubility in benzene with a free hydroxyl group content of 70 mol. % and solubility in aliphatic hydrocarbons with a free hydroxyl content of 40 mol. %, has not been observed previously with other polyvinyl alcohol derivatives and is of theoretical and practical interest.

TABLE 3

Solubility of Triethylsilyl Ethers of Polyvinyl Alcohol

Expt. No.	Si content, mol. %	Solvent: water	methanol	ethanol	acetone	pyridine	dioxane	benzene	ligroin	dichloroethane	chloroform
1	13.7	–	s	–	–	+	+	–	–	s	–
2	19.6	–	+	s	–	+	+	s	–	s	–
3	31.6	–	–	+	+	+	+	+	–	+	+
4	44.4	–	–	–	–	+	+	+	–	+	+
5	61.6	–	–	–	–	+	s	+	+	+	+
6	78	–	–	–	–	–	–	+	+		

Footnote: Plus denotes soluble, minus, insoluble, and s swells.

TABLE 4

Properties of Triethylsilyl Ether

Sample No.	Si content, mol. %	Electrical propt.			Mechanical properties		
		ρ_s	$tg\,\delta$	ε	T_v °C	tensile strength, kg/cm²	relative elongation, %
1	13.7				65	280	13
2	30	$2.5 \cdot 10^{16}$	0.035	5	36	212	64
3	45	$5.5 \cdot 10^{16}$	0.025	4.8	Balsam-like		

For tablets (d = 10 mm; h = 5 mm), pressed from polymers containing from 6 to 30 mol. % of Si, the imbibition during immersion in water for 24 hr decreased from 10 to 0.1%.

When a product containing 61.5 mol. % of Si was hydrolyzed by Price's method with 0.3% NaOH (alcohol solution) in benzene for 6 days at 18°, a precipitate formed and this was dried, dissolved in water, and precipitated with acetone. The product obtained contained 0.8 mol. % of Si, which indicates practically complete hydrolysis of the triethylsilyl groups under these conditions.

Tablets were pressed from the products obtained for studying the thermal properties. The softening point on a block for polymers containing 13-15 mol. % of Si was 125°. However, with an increase in the number of triethylsilyl groups, the polymer became softer at normal temperatures.

As Table 4 shows, with an increase in the degree of substitution, the vitrification point (determined on Marey's apparatus) fell. Films were cast on water and mercury (casting of films on glass was impossible due to the high adhesion of the polymer to glass) for tensile strength testing. Some mechanical and dielectric properties are given in Table 4.

Triethylsilyl ethers of polyvinyl alcohol with a degree of substitution of 30 mol. % and above have a strength which is sufficient for many purposes and quite high dielectric indices.

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*Original Russian pagination. See C. B. translation.

**See C. B. translation.

SYNTHESIS OF INDAN HYDROCARBONS WITH SIDE CHAINS IN THE FIVE-MEMBERED AND BENZENE RINGS

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In previously published work, the syntheses of indan hydrocarbons with substituents in the five-membered [1] or benzene [2] rings were described. The former were synthesized by a reaction proposed by Thiele [3] and modified somewhat by Ruzicka and Peyer [4] in which indene is condensed with ketones in the presence of an alcohol solution of potassium hydroxide. The yield of reaction products, namely, alkyl- and cycloalkylbenzofulvenes, which are intermediates in the synthesis of alkylindans, was 24-40%.

In the present communication we describe syntheses of indan hydrocarbons with substituents in the five- or six-membered ring and also with substituents in both rings.

1-Cyclohexylindan. After distillation on a column with an efficiency of 12 theoretical plates*, the starting indene had b. p. 91° at 46 mm, n^{20}_D 1.5761; d^{20}_4 0.9956, which agrees with literature data [5]. After distillation, the cyclohexanone of grade X had b. p. 151-152° at atmospheric pressure and n^{20}_D 1.4515.

1-Cyclohexylindan was obtained analogously to 1-cyclopentylindan [2] by condensation of indene (147 g) in ether with cyclohexanone (62 g) in the presence of potassium hydroxide (16 g) in methanol (30 ml) with heating and continuous stirring.

The cyclohexanone was added to the indene rapidly and the alkali solution slowly in drops. When the whole of the alkali had been added, stirring was continued for a further 2 hr. As the doubly unsaturated hydrocarbon formed was unstable in air, the synthesis and distillation of ether from the reaction product were carried out in a stream of nitrogen. Instead of molar ratios of indene to ketone of 1 : 1, as we used in previous syntheses [1, 2], we used 2 : 1. The amount of alcoholic alkali was the same as in previous syntheses, namely 12 g of potassium hydroxide in 28 ml of methanol to 1 mole of indene [4].

Part of the reaction product was distilled on a column. The crystalline fraction of cyclohexylbenzofulvene thus obtained was yellow (b. p. 127-130° at 1 mm) and had n^{20}_D 1.6159.

	Found %:	C 91.88;	91.75;	H 8.11;	8.19
$C_{15}H_{16}$	Calculated %:	C 91.78;		H 8.22	

The yield of the fraction, calculated on the ketone used, was 54%. The remainder of the product after distillation of the ether was hydrogenated over Raney nickel at an initial hydrogen pressure of 150 atm and normal temperature. Two distillations of the hydrogenation product on a column yielded a colorless hydrocarbon boiling at 121° at 2 mm.

*The same column was used in all subsequent distillations.

Found %: C 90.05; 90.01; H 10.04; 10.08

$C_{15}H_{20}$. Calculated %: C 89.93; H 10.07

Molecular weight: found 200 and 200, calculated 200.

The properties of 1-cyclohexylindan are given in Table 1.

TABLE 1

Properties of Indan Hydrocarbons

Hydrocarbon	B.p., °C/mm	Solid. point (glass), °C	d_4^{20}	n_D^{20}	Aniline point (max), °C	MR found	MR calc.
1-Cyclohexylindan $C_{15}H_{20}$	121°/2	—58	0,9917	1,5464	—12	63,99	63,47
1-Isopropylindan $C_{12}H_{16}$	86 — 87°/4	—65	0,9336	1,5219	—14,8	52,42	51,82
	87 — 88°/4	—65	0,9350	1,5238	—14,8	52,42	51,82
5-Decylindan $C_{19}H_{30}$	160 — 161°/4	—65	0,9017	1,5066	11,0	85,23	84,14
1-Isopropyl-5-tert-butylindan $C_{16}H_{24}$	112 — 113°/1,5	—35	0,8967	1,5050	18,0	71,56	70,29
1-Isopropyl-5,7-di-tert-butylindan $C_{20}H_{30}$	139 — 140°/1,5	—26	0,8987	1,5090	38,0	90,52	88,76

1-Isopropylindan. 1-Isopropylindan, which has been described previously [1], was reprepared in large amounts as a starting material for the synthesis of indan hydrocarbons with two alkyl chains. For the reaction we used 362 g of indene and 90 g of acetone, which corresponds to a ratio of indene to acetone of 2 :1. The reaction product was hydrogenated over Raney nickel at an initial hydrogen pressure of 150 atm and room temperature and then distilled three times on a column. This yielded two fractions of hydrocarbon boiling over two-degree ranges with the same composition, but different densities and refractive indices (see Table 1).

For the fraction with b. p. 86-87°at 4mm: found% C 89.92; 89.99; H 10.06; 9.98 and MR 52.42.

For the fraction with b. p. 87-88°at 4mm: found% C 89.92; 89.87; H 10.04; 10.02 and MR 52.42.

Calculated for $C_{12}H_{16}$ %: C 89.93; H 10.07 and MR 51.82.

The properties of the hydrocarbons are given in Table 1. The investigation of the two fractions obtained is continuing.

As in previous cases [2], the alkylation of indan with unsaturated hydrocarbons in the presence of 92% sulfuric acid was used for the preparation of indan hydrocarbons with alkyl substituents in the benzene ring.

5-Decylindan. The indan required for the synthesis was prepared by hydrogenation of the indene mentioned above in an autoclave over Raney nickel at an initial hydrogen pressure of 150 atm and room temperature. After two distillation, the indan had b. p. 173-174° at 751 mm, n^{20}_D 1.5389; d^{20}_4 0.9629, which correspond to literature data [6]. The decene was prepared from n-decanol (b. p. 109-110° at 9 mm, n^{20}_D 1.4371; d^{20}_4 0.8306) by dehydrogenation at 370° over aluminum oxide. After two distillations on a column and then over metallic sodium, it had b. p. 172-173° at 745 mm, n^{20}_D 1.4257; d^{20}_4 0.7439.

5-Decylindan was prepared by alkylation of indan with decene in the presence of sulfuric acid. With continuous mechanical stirring, 70 g of decene and 98 g of 92% sulfuric acid were gradually added dropwise to 118 g of indan. As the reaction products evolved heat, they were cooled with ice water. In contrast to previous syntheses [2], the molar ratio of indan to decene to sulfuric acid was 2 : 1 : 2. After the required amount of olefin had been added, the mixture was stirred for a further 1.5 hr. Two distillations of the hydrocarbon obtained on a column yielded 98 g of a fraction with b. p. 160-161° at 4 mm, which corresponds to a decylindan yield of 76% on decene.

The properties of the hydrocarbon obtained are given in Table 1.

	Found %:	C 88.34;	88.30;	H 11.76;	11.75
$C_{19}H_{30}$.	Calculated %:	C 88.29;		H 11.71	

Molecular weight: found 259 and 257, calculated 258. It is most probable that the side chain enters position 5 in such a synthesis [7].

1-Isopropyl-5-tert-butylindan and 1-isopropyl-5, 7-di-tert-butylindan. 1-Isopropyl-5-tert-butylindan was prepared analogously to 5-decylindan by alkylation of 1-isopropylindan with isobutylene in the presence of 92% sulfuric acid; with continuous stirring, 14 g of sulfuric acid was added dropwise to 22 g of 1-isopropylindan (b. p. 87-88° at 4 mm, n^{20}_D 1.5238; d^{20}_4 0.9350) while 4 g of isobutylene was passed in at 2-3 liter/hr. The molar ratio of isopropylindan to isobutylene to sulfuric acid was 2 : 1 : 2. After the addition of the isobutylene and sulfuric acid, the mixture was stirred for a further 1.5 hr.

The hydrocarbon layer was treated in the usual way and distilled twice on a column. This yielded a fraction with b. p. 112-113° at 1.5 mm.

	Found %:	C 88.67;	88.65;	H 11.35;	11.25
$C_{16}H_{24}$.	Calculated %:	C 88.82;		H 11.18	

Molecular weight: found 215 and 216, calculated 216.

The final yield of this hydrocarbon, calculated on isobutylene, was 35%. The properties of the hydrocarbon are given in Table 1. The tertiary butyl group should be in position 5 in the indan, as was demonstrated previously [7].

From the high-boiling reaction products, we isolated a fraction with b. p. 139-140° at 1.5 mm. The properties of the hydrocarbon are given in Table 1.

	Found %:	C 88.03;	88.22;	H 11.89;	11.82
$C_{20}H_{32}$.	Calculated %:	C 88.15;		H 11.85	

Molecular weight: found 272 and 272; calculated 272.

Due to the fact that the yield of this fraction was about 3 g, it was impossible to distill it on a column, but judging by the data obtained, together with a dialkylindan, the alkylation of 1-isopropylindan with isobutylene forms a small amount of trialkylindan.

It may be assumed that the tert-butyl groups are most probably in positions 5 and 7 as two tert-butyl groups do not usually enter ortho positions.

All the hydrocarbons described were treated with sulfuric acid under identical conditions to obtain comparable data on their capacity for sulfonation. Those which were resistant to the action of 98% sulfuric acid were treated with 100% sulfuric acid. As was to be expected, 1-isopropyl-5, 7-di-tert-butylindan was most resistant to the action of the acid. Its volume did not change when it was treated with three volumes of 100% sulfuric acid for 30 min.

Treatment of 1-isopropyl-5-tert-butylindan with two volumes of 100% sulfuric acid for 30 min resulted in 20% sulfonation. 1-Isopropylindan, 1-cyclohexylindan, and 5-decylindan were sulfonated completely after 1 hr by one volume of 98% sulfuric acid.

1-Cyclohexylindan, 1-isopropyl-5-tert-butylindan, 1-isopropyldi-tert-butylindan, and 5-decylindan were prepared for the first time.

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TELOMERIZATION OF ORGANOCYCLOSILOXANES

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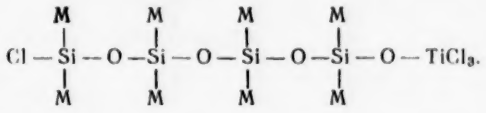
Telomerization [1] is widely used for the synthesis of various organic compounds by polymerization of unsaturated organic compounds in the presence of substances which terminate the growth of the molecular chain. Various organic compounds (halogenated paraffins [2,3,4], alcohols [5], acids [6], etc.) and a number of organosilicon compounds containing the Si—H bond [7-9] are used as substances for terminating the growing polymer chain. It is of great theoretical and practical interest to realize telomerization reactions giving oligomers with inorganic main chains, clothed with organic groups. No such reactions have been described in the literature and the lack of heteroorganic monomers containing double bonds between the heteroelement and oxygen, which are capable of polymerization, makes it possible to use experience of telomerization reactions which have been studied thoroughly in the synthesis of organic telomers.

One of us previously showed that the action of titanium tetrachloride on octamethylcyclotetrasiloxane produces ring cleavage with the formation of the compound:



This compound was formed as a result of cleavage of the siloxane ring and the addition of chlorine and trichlorotitanium groups [10].

To achieve telomerization reactions, we used rings of inorganic atoms clothed with organic groups. Octamethylcyclotetrasiloxane was taken as the cyclic compound and dimethyldichlorosilane as the substance terminating the molecular chain. Experiments showed that dimethyldichlorosilane is not only a reagent for terminating the growth of a molecular chain, but also a compound which polymerizes octamethylcyclotetrasiloxane.

By a study of the reaction of octamethylcyclotetrasiloxane and dimethyldichlorosilane it was established that ring opening occurs at a high rate at 200-250° in the absence of catalysts. Thus, the reaction between octamethylcyclotetrasiloxane and dimethyldichlorosilane in a molar ratio of 2:1 was complete after 3 hr at 250°. This yielded oligomers whose composition corresponded to compounds described by the reaction given below.

$$n\,(M_2SiO)_4 + M_2SiCl_2 \rightarrow Cl - (- M_2SiO -)_{4n} - M_2SiCl.$$

Repeat experiments readily gave reproducible results in accordance with the given reaction. The experiments gave about 75% of reaction products distilling up to 260° at 3 mm and only about 25% of the products boiled above this temperature. Fractionation yielded α,ω-dichlorodecamethylpentasiloxane (n = 1) in 16.7% yield, α,ω-dichlorooctadecamethylnonasiloxane (n = 2) in 20.0% yield, and α,ω-dichlorohexacosamethyltridecasiloxane (n = 3) in 7.7% yield. The physical properties of the products isolated are given in Table 1.

TABLE 1

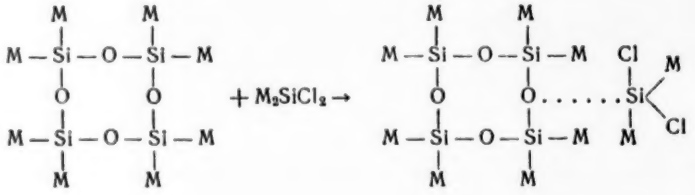
Physical Properties of Telomers

Compound	B.p., °C/mm	n_D^{20}	d_4^{20}	MR	
				calc.	found
1. $Cl[(CH_3)_2SiO]_4(CH_3)_2SiCl$	220–221° *	1,4032	1,0048*	102,68	103,22
2. $Cl[(CH_3)_2SiO]_8(CH_3)_2SiCl$	176–178°/3	1,4065	0,9945	179,06	178,56
3. $Cl[(CH_3)_2SiO]_{12}(CH_3)_2SiCl$	246–248°/3	1,4060	0,9885	253,85	253,13

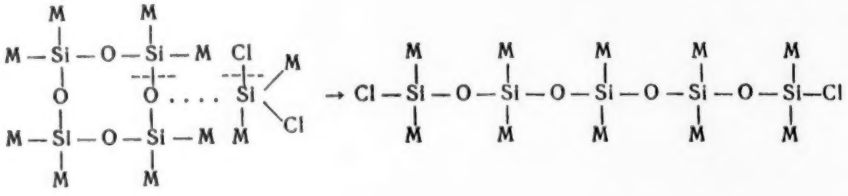
*Literature data [11]: M.p. 138°/20 and d_4^{20} 1.005.

The formation of oligomers containing 5,9, and 13 silicon atoms in the molecule indicates successive addition of octamethylcyclotetrasiloxane molecules to dimethyldichlorosilane.

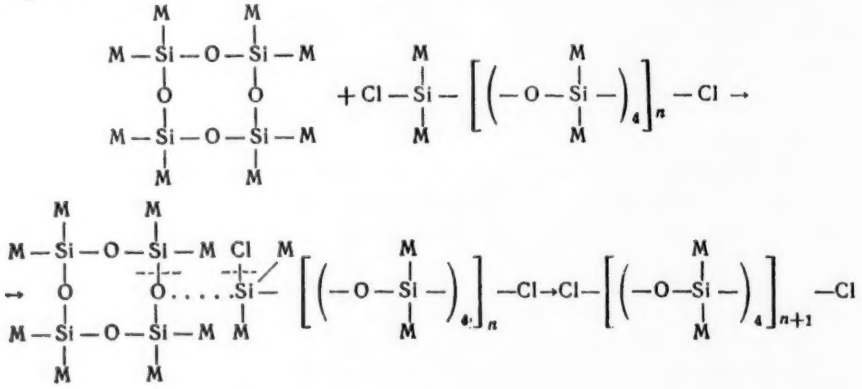
The beginning of the reaction was apparently coordination of one of the oxygen atoms of octamethylcyclotetrasiloxane with the silicon atom of dimethyldichlorosilane.



The weakening of the Si–O bond in octamethylcyclotetrasiloxane resulted in cleavage of the strained ring with the addition of chlorine to the silicon atom and dimethylchlorosilane to the oxygen.



The further growth of the chain was probably associated with the coordination of the terminal silicon atoms and the oxygen of the cyclic product with subsequent ring cleavage and the formation of linear α,ω-dichlorodimethylsiloxane according to the reaction:



At the present time this reaction is being studied with other inorganic rings, clothed with organic groups, and other reagents for terminating the molecular chain are also being investigated.

Experimental

For the syntheses we used octamethylcyclotetrasiloxane with b.p. 174-176° (molecular weight 296.6) and dimethyldichlorosilane containing 55.7% of Cl (molecular weight 129.08).

TABLE 2

Fraction No.	B.p., °C/mm	No. of Si atoms	Chlorine content		Yield	
			calc.	found*	g	% on mixt.
1	up to 200°	—	—	—	32,9	11,2
2	200—220°	5	16,68	16,48	49,4	16,7
3	130—140°/3	—	—	13,95	6,0	2,0
4	140—155°/3			12,65	16,0	5,5
5	155—170°/3			11,39	9,4	3,2
6	170—210°/3	9	9,83	9,69	58,0	20,0
7	210—220°/3			8,27	8,9	3,0
8	220—230°/3			7,41	9,2	3,1
9	230—260°/3	13	6,96	6,81	22,6	7,7
			Losses		4,9	1,9
			Total		293	100

*The average data for 2 determinations are given.

Reaction of octamethylcylotetrasiloxane with dimethyldichlorosilane. Into a dry, 0.5-liter, stainless steel autoclave was placed a mixture of 55.7 g (0.435 mole) of dimethyldichlorosilane and 258 g (0.87 mole) of octamethylcyclotetrasiloxane. The apparatus was heated to 250° over a period of 1 hr and kept at this temperature for 3 hr. At the beginning of heating, the pressure in the apparatus rose to 8-10 atm and then fell to 2-3 atm. When the apparatus had cooled, in one experiment we obtained 293 g of product which was distilled from a flask with a pear fractionating column at first under atmospheric pressure and then at 3 mm. The experimental data are given in Table 2.

Two distillations of fractions No. 2, 6, and 9 (Table 2) yielded pure products with the compositions $Cl-[Si(CH_3)_2O]_nSi(CH_3)_2-Cl$, where n = 4, 8, and 12, whose physical properties are given in Table 1 and analysis data in Table 3.

TABLE 3

$Cl[(CH_3)_2SiO]_n-(CH_3)_2SiCl$

Compound	B.p., °C/mm	Cl, %		H, %		C, %		Si, %	
		calc.	found	calc.	found	calc.	found	calc.	found
$Cl[(CH_3)_2SiO]_4(CH_3)_2SiCl$	220—221°	16,68	16,58 16,43	7,1	7,00 7,09	28,21	28,67 28,67	32,96	33,30 33,36
$Cl[(CH_3)_2SiO]_8(CH_3)_2SiCl$	176—178°/3	9,83	9,49 9,45	7,53	7,38 7,26	29,93	29,82 29,66	34,97	34,96 35,24
$Cl[(CH_3)_2SiO]_{12}(CH_3)_2SiCl$	246—248°/3	6,96	6,96 6,86	7,71	7,65 7,62	30,65	30,54 30,64	35,80	35,90 35,95

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*See C. B. translation.

INVESTIGATION OF THE THERMODYNAMICS OF LOWER TUNGSTEN OXIDES THROUGH THE EMF AT HIGH TEMPERATURES

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The equilibrium of the reduction of tungsten oxides by hydrogen, which has been studied previously [1, 2], makes it possible to calculate thermodynamic functions of the formation of tungsten trioxide from the elements.

The inadequate accuracy of the measurement of high equilibrium constants and the dependence of the accuracy of the calculated data on the values for water vapor make it desirable to determine the thermodynamic functions of the formation of tungsten oxides from the elements by another, independent method. For this purpose we chose the method of electromotive forces, whose application to oxide electrodes has been described in [3-6]. The procedure in these papers was modified somewhat. Our experiments were carried out in vacuum, in a specially designed metal cell, which was insulated with fused quartz. The furnace temperature was measured with a platinum–platinorhodium thermocouple and a potentiometer. As the electrolyte we used a solid solution of 0.85 ZrO_2 + 0.15 CaO, which has anion conductivity.

Over the temperature range 900-1230° K, we measured the emf of cells of the type WO_x [ZrO_2CaO] $Fe_{0.95}O$, Fe, where x = 2.719 (1); 2.66(2); 2.39(3); 1.90(4); 1.69(5) and 1.45(6). Oxides of the given composition were obtained by hydrogen reduction of the low temperature modification of α-WO_3 [2]. The first three compositions correspond to mixtures of the phases $WO_{2.72}$ and WO_2 and the last compositions correspond to mixtures of WO_2 and W. The mixture $Fe_{0.95}O$ + Fe served as a reference electrode.

The experimental values of the emf of cells 1-3 and 4-6 were described by equations (1) and (2), respectively:

$$E_1 = 76.8 - 0.06T \text{ (mv)} \quad (1)$$

with the equation describing the mean experimental values with an accuracy of ± 1.5 mv;

$$E_2 = -6.68 + 0.045T \text{ (mv)} \quad (2)$$

with the equation describing the mean experimental values with an accuracy of ± 0.5 mv.

A combination of ΔG of the cells (1,2), calculated from the known equation $G_{cell} = -zFE_{cell}$, and ΔG of formation of $Fe_{0.95}O$ from the elements (Lange's data [7]) gives for the reaction

$$^1/_2W + {}^1/_2O_2 = {}^1/_2WO_2 \quad (I)$$

the equation

$$\Delta G_1 = -68542 - 7.21\,T \lg T + 1.26\cdot10^{-3}T^2 - 0.47\cdot10^5 T^{-1} + 40.62T \quad (943-1230^\circ K).$$

The values of ΔG_1 over the temperature range 973-1273°K calculated from this equation and the values of $\Delta G'_1$ for reaction (I) for these temperatures, which we obtained previously [2] from equilibrium data, are given in Table 1. For the reaction

$$^{100}/_{72}\,WO_2 + {}^1/_2\,O_2 = {}^{100}/_{72}\,WO_{2,72} \qquad (II)$$

we have the equation

$$\Delta G_2 = -65308 - 7.21\,T \lg T + 1.26\cdot10^{-3}T^2 - 0.47\cdot10^5 T^{-1} + 39.93\,T \quad (900-1173^\circ K).$$

The values of ΔG_2 over the range 923-1173°K, calculated from this equation and the values of $\Delta G'_2$ for reaction (II) for these temperatures, which we obtained previously [2] from equilibrium data, are given in Table 2.

TABLE 1

Temp., °K	$-\Delta G_1$, kcal	$-\Delta G_1'$, kcal
973	48,8±1,5	49,5
1073	47,0±1,5	47,5
1173	45,2±1,5	45,4
1273	43,3±1,5	43,3

TABLE 2

Temp., °K	$-\Delta G_2$, kcal	$-\Delta G_2'$, kcal
923	47,1±0,5	47,2
1023	45,4±0,5	45,4
1123	43,7±0,5	43,6
1173	42,8±0,5	42,7

A combination of reactions (I) and (II) correspondingly gives for the reaction

$$W + 1{,}36\,O_2 = WO_{2,72} \qquad (III)$$

the equation

$$\Delta G_3 = -184106 + 9.23\,T \lg T + 3.43\cdot10^{-3}T^2 - 1.28\cdot10^5\,T^{-1} + 109.9T.$$

For calculating the standard thermodynamic values, we used the heat capacities of O_2 and W given in [8] and for WO_2 we used the equation $c_p = 17.83 + 1.89\cdot10^{-3}T - 3.342\cdot10^5\,T^{-2}$ (accuracy ± 3%), which we derived from the values of c_{p298} for WO_2 [9], the values of c_p for solids at the conversion temperature, and the mean equations for the oxides UO_2 [10], VO_2 [11], and ThO_2 [11], which have values of c_{p298} similar to that of WO_2.

TABLE 3

$-\Delta H^\circ_{298}$, kcal	$-\Delta G^\circ_{298}$, kcal	$-\Delta S^\circ_{298}$, e.u.	S°_{298}, e.u.	Source
134±1	122,0	41		[15]
134,5±5			15±2,5	[11]
137±1			19,7±1	[16]
140,94±0,2				[17]
136,6±2	124,0±2	41,7±1,5	15±1,5	Our data obtained by the emf method

By using these values, we obtained for the reaction

$$W + O_2 = WO_2 \qquad (IV)$$

the equation

$\Delta G_T = -136.6 - T\,(4.66\,M_0 + 0.21M_1 - 2.44M_{-2}) + 41.7T$

(M_0, M_1, M_{-2} are the coefficients of the Temkin–Shvartsman equation [12]), whence

$$\Delta H^0_{298} = -136{,}6 \pm 2 \text{ kcal};$$
$$\Delta S^0_{298} = -41{,}7 \pm 1{,}5 \text{ e.u.}$$
$$\Delta G^0_{298} = -124 \pm 2 \text{ kcal.}$$

By using the values of S^0_{298} for W [13] and O_2 [14], we obtained for WO_2

$$S^0_{298} = 15{,}0 \pm 1{,}5 \text{ e.u.}$$

Some literature data for the thermodynamic functions of the formation of WO_2 from the elements under standard conditions are given in Table 3 for comparison.

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EFFECT OF AGEING TIME ON THE FORMATION AND COMPOSITION OF THE γ'-PHASE IN ALLOYS OF THE SYSTEM Ni – Cr – W – Al – Ti

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The γ'-phase, which is liberated during the decomposition of the main solid solution, is the phase which mainly determines the high properties of a whole series of alloys based on nickel. According to the data of many authors, the γ'-phase is a solid solution based on the compound Ni_3Al in which, in addition to titanium, other elements present in the alloy may dissolve [1, 2]. Crystals of the γ'-phase have a face-centered cubic lattice, whose period depends on the composition of the alloy. The lattice period of the pure compound Ni_3Al equals 3560 kX.

The literature contains reports that in some alloys, the γ'-phase is metastable and changes into the phase Ni_3Ti on prolonged ageing. N. I. Blok et al. [3] have reported such a conversion in alloys of the system Ni–Cr–Al–Ti. According to the data of A. Ya. Snetkov, the γ'-phase is metastable in alloys which contain a large amount of titanium. The alloys investigated were prepared by L. I. Pryakhina and O. V. Ozhimkova and after they had been kept at 1200° for 134 hr, they were quenched at 1200° in water and then aged at 900°. The ageing time was from 0 to 10,000 hr.

According to the microstructural analysis data of L. I. Pryakhina and O. V. Ozhimkova, the alloys investigated were two-phase and consisted of a γ-solid solution and a γ'-phase. With an increase in ageing time, in addition to formations with a rounded shape, there appeared formations in the form of streaks on the polished section. This may be explained either by a change in form of the separated phase or by conversion of the γ'-phase to the Ni_3Ti phase.

For studying the composition and structure of phases formed in the alloys investigated, together with other methods, we carried out a special investigation based on the electrolytic isolation of excess phases. For the isolation of the γ'-phase from the alloys we used an electrolyte which we developed previously [4] and which consisted of 50 ml of HNO_3 and 20 ml of $HClO_4$ in 1000 ml of water. The anode powders isolated were subjected to chemical and x-ray structural analyses. A sample of the powder was dissolved in aqua regia and then the tungsten separated hydrolytically. The filtrate after separation of the tungsten was transferred to a graduated flask and aliquot portions used to determine aluminum, nickel, and chromium.

For the determination of small amounts of chromium in the presence of large amounts of other elements, it was necessary to check chemically the possibility of determining gamma amounts of chromium with diphenylcarbazide under these conditions. On the basis of the work, we developed efficient conditions for determining chromium. Due to the fact that the large amount of tungsten present in the anode powders (~20%) trapped part of the titanium during the precipitation, the titanium was determined on a separate sample (0.01g). H_3PO_4 (d 1.70) was added to bind the tungsten in solution. The results of chemical analysis are given in Table 1.

To study the conditions of electrochemical solutions of the alloys, we isolated the excess phase in an electrolyte which we proposed previously [5, 6] and which consisted of 35g of citric acid, 5 g of $(NH_4)_2SO_4$, and 15 ml of HNO_3 in 1000 ml of water.

The chemical composition of the phase isolated in this electrolyte is also given in Table 1.

TABLE 1

Chemical Composition of γ'-Phase

Expt. No.	Ageing time, hr	Ni	Al	Ti	Cr	W	Sum of elements	$\frac{Ni}{\Sigma Al, Ti, Cr}$
γ-Phase isolated in electrolyte consisting of 50 ml of HNO_3, 20 ml of $HClO_4$, and 1000 ml water								
8	0	65,20	6,33	3,26	4,26	20,92	99,97	
		69,03	14,58	4,23	5,09	7,07	100,00	2,9
1	100	65,31	6,46	2,80	3,88	21,50	99,95	
		69,46	14,95	3,64	4,66	7,30	100,10	3,0
5	500	64,57	7,05	3,33	3,35	20,98	99,95	
		68,85	15,25	4,66	4,17	7,07	100,00	2,9
11	1000	65,51	6,75	2,96	3,66	20,98	99,86	
		69,22	15,51	3,83	4,36	7,07	99,99	2,9
16	3000	65,32	6,65	3,61	3,51	21,02	100,11	
		68,85	15,25	4,66	4,17	7,07	100,00	2,9
3	5000	65,28	6,60	3,80	3,15	21,08	99,91	
		68,87	15,14	4,91	3,75	7,33	100,01	2,9
4	10000	65,30	6,56	3,90	3,20	21,04	100,00	
		68,98	15,07	5,04	3,81	7,09	99,99	2,9
γ'-Phase isolated in an electrolyte consisting of 35 g of citric acid, 5 g of $(NH_4)_2SO_4$, 15 ml of HNO_3, and 1000 ml of water								
15	1000	72,53	8,15	4,19	3,71	11,29	99,87	
		70,30	17,18	4,98	4,06	3,49	100,01	2,68
22	3000	72,26	8,00	3,94	3,93	11,84	99,97	
		70,34	16,95	4,70	4,32	3,68	99,99	2,71
1	5000	72,87	8,37	3,80	2,77	12,07	99,88	
		70,95	17,73	4,53	3,04	3,75	100,00	2,80
2	10000	72,69	8,27	4,14	2,96	11,83	99,94	
		70,65	17,49	4,93	3,25	3,68	100,00	2,75

Note. The weight percent is given above the line and the atomic percent below the line.

As the data presented show, the composition of the γ'-phase remained largely unchanged with the change in the ageing time of the alloy from 0 to 10,000 hr. The ratio Ni to ΣAl, Ti, Cr, in atomic percents, equalled approximately 3.

The ratio $\frac{Ni}{\Sigma Al,Ti,Cr}$ in the phase isolated in an electrolyte consisting of 50 ml of HNO_3 and 20 ml of $HClO_4$ in 1000 ml of water was closer to 3 than in the phase isolated in an electrolyte consisting of 35 g of citric acid, 5 g of $(NH_4)_2SO_4$, 15 ml HNO_3, and 1000 ml of water. This indicates that the first electrolyte is more suitable for isolation of the γ'-phase.

According to x-ray analysis data* all the anode powders contained γ'-phase with a lattice parameter a = 3.573 kX, which was a solid solution based on the compound Ni_3Al. Superlattice lines characteristic of the pure compound Ni_3Al were not detected. X-ray diffraction patterns of all powders isolated from quenched alloys and

* The x-ray structural investigation was carried out by A. Ya. Snetkov.

from alloys aged for up to 10,000 hr showed weak lines of a phase whose nature was not established. No lines corresponding to a γ solid solution and the compound Ni_3Ti were detected.

For studying the distribution of elements between the phases, we drew up a balance of electrolysis products for an alloy aged for 1000 hr and calculated the content of the elements in weight percent in the γ nickel solid solution and in the γ'-phase.

The electrolytic method we used for isolating excess phases made it possible to establish the presence of a metalloid γ'-phase in the 5-component nickel alloys investigated and to study the effect of prolonged ageing on the composition and structure of this phase.

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*Original Russian pagination. See C.B. translation.

INTRAMOLECULAR REVERSIBLE CYCLIZATION OF AMIDES OF 8-(2^1, 3^1, (CO), 6^1, 5^1 (CO)-DIBENZOYLENEPYRIDYL-4^1) -1-NAPHTHOIC ACID

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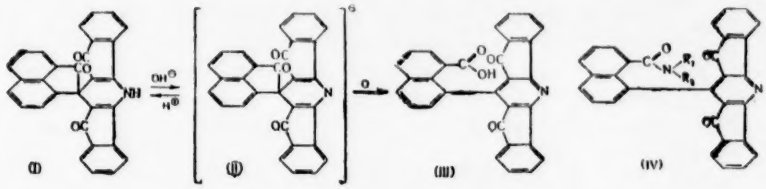
The condensation product of 1,3-indandione and acenaphthenequinone, diindandionylacenaphthene-1, is converted by the action of ammonia into acenaphthenone-1-spiro-(2:4^1)-2^1, 3^1 (CO), 6^1, 5^1 (CO)-dibenzoylene-1^1, 4^1-dihydropyridine (I) [1]. It dissolves in alcoholic alkali with a green color, which is characteristic of many dibenzoylenedihydropyridines. We recently developed a convenient method for preparing this compound and studied its oxidation: with cleavage of the acenaphthene ring there is formed 8-(2^1, 3^1 (CO), 6^1, 5^1 (CO)-dibenzoylenepyridyl-4^1)-1-naphthoic acid (III). We also prepared some derivatives of this acid: salts, esters, and the acid chloride*. a) $R_1 = R_2 = H$; b) $R_1 = C_2H_5$; $R_2 = H$; c) $R_1 = R_2 = C_2H_5$; d) $R_1 = C_2H_5$; $R_2 = CH_3CO$; e) $R_1 = C_2H_5$, $R_2 = p\text{-}O_2N\cdot C_6H_4CO$.

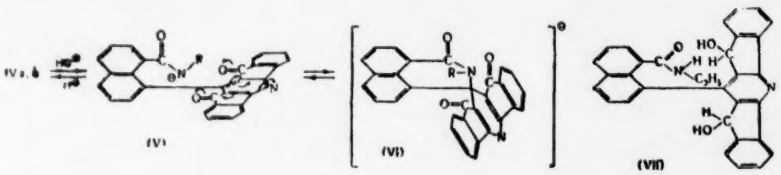


The action of ammonia and primary and secondary amines on the acid chloride of acid III yielded its amides (IV a, b, c). Like all the other derivatives of acid III, they had a yellow color in neutral and acid media. However, those amides which have at least one hydrogen atom at the amide nitrogen (IV a, b) dissolved in alcoholic alkali with an intense violet color; the substance was recovered unchanged when the solution was acidified. The sodium salt of amide IV was isolated in the pure form. The diethylamide (IV c) did not dissolve in alcoholic alkali and its absorption spectrum in the ultraviolet and visible regions did not change after alkali had been added. The N-ethyl-N-acetyl- and N-ethyl-N-p-nitrobenzoylamides (IV d, e) dissolved slowly under the action of alcoholic alkali and gradually acquired a violet color, which was evidently associated with elimination of the acyl group and regeneration of the ethylamide (IV b).

The phenomenon described cannot be ascribed solely to the amide group of naphthamide as the latter does not give such a color and the nature of its spectrum (Fig. 1) does not change when alkali is added, while amides IV a and b lose the absorption spectrum characteristic of all aryldibenzoylpyridines (Fig. 2) when dissolved in alcoholic alkali. The violet color produced when amides IV a and b are dissolved in alkalis appears only if the

* The work will be reported in Journal of General Chemistry, Vol. 30, No. 6.

carbonyl groups are retained; the color was not given by the dioxime of the ethylamide and the reduction product of the ethylamide (VII). From this it follows that in the presence of alkali, the two parts of the molecule, the naphthamide and the dibenzoylenepyridine parts, react with the formation of a violet anion VI, which is reconverted into amide IV on acidification.



In the pyridine molecule, the electron cloud is displaced toward the nitrogen and fractional positive charges appear on the α- and γ-carbons. They are the reason for nucleophilic substitutions in the pyridine ring. In our case, the carbonyl groups of benzoylene in the β position further increase the electrophilic character of the α- and γ-carbons.

At the amide nitrogen, the free pair of electrons is displaced toward the carbonyl group and therefore the nucleophilic character of the nitrogen is reduced. However, in an alkaline medium amides are capable of losing a proton and acquiring a strong nucleophilic character. This is indicated by polarographic investigation of amides [2]. The same process is apparently the reason for cyanoethylation of amides in the presence of alkali agents [3, 4]. It is clear that for this to occur there should be at least one hydrogen atom at the amide nitrogen.

It is not by chance that no cases have been found up to now of the reaction of pyridine with acid amides either in neutral or alkaline media. In our case, the amide nitrogen and the electrophilic γ-carbon of pyridine are in a very favorable position: together with the four carbon atoms connecting them they form a system of 6 atoms, which tends to coplanarity and the formation of a 6-membered ring. Such a possibility of a transannular reaction [5] appears in an alkaline medium. The reaction product (VI) essentially corresponds to the intermediate product of nucleophilic substitution in pyridine [6] or aromatic nitro compounds [7, 8], but it may be stabilized in only one direction, namely the regeneration of the starting material (IV). These changes occur readily and rapidly at room temperature.

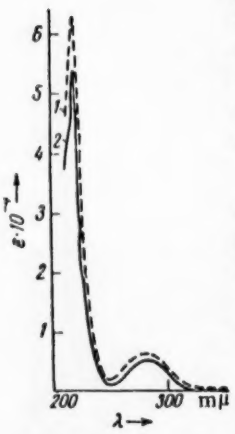


Fig. 1. Ultraviolet absorption spectra of α-naphthamide: 1) in methanol; 2) in alkaline methanol.

In structure, the reaction product (VI) is very similar to the anion of benzoylenedihydropyridine (II). This similarity in structure is reflected in the absorption spectra (Figs. 2 and 3). In a neutral medium, the absorption spectrum of the amide (IV a) and the ethylamide (IV b) differ substantially from the absorption spectrum of I. All this indicates nucleophilic, reversible intramolecular addition of amides to dibenzoylenepyridine. It is interesting to note that a communication appeared recently on the reversible addition of an active methylene group to the electrophilic C_9 atom of acridine [9].

It should be noted that there are some other peculiarities of the amides described: for example, they are extremely resistant to hydrolysis reactions, they could not be prepared from esters of acid III by ammonolysis, and they were very difficult to burn; accurate microanalysis results for nitrogen could be obtained only with the use of nickel oxide.

Experimental

Amide of 8-[2¹, 3¹ (CO), 6¹, 5¹ (CO)-dibenzoylenepyridyl-4¹]-1-naphthoic acid (IV a). To a hot solution of 3.4 g of the acid chloride of acid III in 170 ml of dry dioxane was added 40 ml of 25% ammonia in small portions. The following day, 350 ml of water was added to the solution, which was then acidified. The precipitate was suspended in 100 ml of a saturated $NaHCO_3$ solution and separated on the following day. This yielded 2.8 g of a yellow substance with m. p. 314-316° (from chlorobenzene or glacial acetic acid). The substance dissolved in an aqueous alcohol solution of alkali with a blue-violet color.

	Found %:	N 6.14
$C_{30}O_{16}O_3N_2$.	Calculated %:	N 6.19

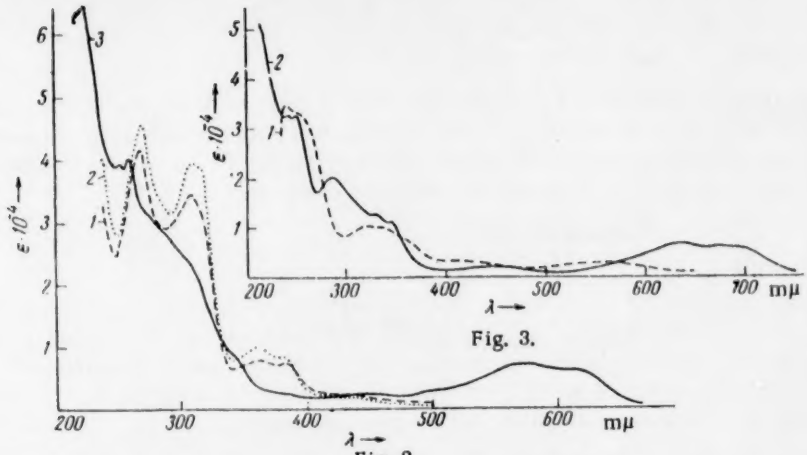


Fig. 3.

Fig. 2.

Fig. 2. Ultraviolet absorption spectra of derivatives of the acid III: 1) ethylamide (IV b) in $CHCl_3$; 2) ethyl ester of III in $CHCl_3$; 3) ethylamide in alkaline methanol (VI).

Fig. 3. Ultraviolet absorption spectra of acenaphthenonedibenzoylenedihydropyridine (I): 1) in $CHCl_3$; 2) in alkaline methanol (II).

Sodium salt of amide (VI). The amide was boiled in 0.5% NaOH solution, the solution filtered, and 20% NaOH solution slowly added to the filtrate to give a 1% NaOH solution. This precipitated fine, dark blue, laminar crystals, which decomposed at 275-280°.

	Found %:	N 5.87; Na 4.90
$C_{30}H_{15}O_3N_2Na$.	Calculated %:	N 5.90; Na 4.85

Ethylamide of 8-[2¹, 3¹ (CO), 6¹, 5¹ (CO)-dibenzoylenepyridyl-4¹]-1-naphthoic acid (IV b). To 10 g of the acid chloride of acid III in 350 ml of anhydrous dioxane were added 10.38 g of $C_2H_5NH_2 \cdot HCl$ and 5.1 g of NaOH and the solution heated on a water bath for 2 hr, diluted with water, and acidified. The precipitate was treated twice with 500 ml of 2% Na_2CO_3 and the residue recrystallized from glacial acetic acid. This yielded 8 g of a yellow substance with m. p. 320°. The product dissolved in an aqueous alcohol solution of alkali with a blue-violet color.

	Found %:	N 5.81
$C_{32}H_{20}O_3N_2$.	Calculated %:	N 5.83

Oxime formation. A mixture of 0.75 g of ethylamide (IV b), 10 ml of anhydrous pyridine, and 2 g of $NH_2OH \cdot HCl$ was heated for 2 hr on a water bath and poured into 100 ml of hydrochloric acid (1 : 1). The precipitate dissolved in 100 ml of 2.5% NaOH and the filtrate acidified. This yielded light yellow needles (from alcohol) with m. p. 290°, which dissolved in aqueous alkali with a yellow color.

	Found %:	N 10.74
$C_{32}H_{22}O_3N_4$.	Calculated %:	N 10.97

Acetylation. The ethylamide (IV b) was boiled for 6 hr in acetic anhydride and the product recrystallized from benzene to give yellow platelets (IV d) with m. p. 263° (from benzene).

	Found %:	N 5.12
$C_{34}H_{22}O_4N_2$.	Calculated %:	N 5.36

p-Nitrobenzoylation. A mixture of 0.5 g of ethylamide (IV b), 2 g of p-nitrobenzoyl chloride, and 5 ml of anhydrous pyridine was boiled for 2 hr and then poured into 50 ml of water and the precipitate purified by treatment with 100 ml of 5% Na_2CO_3. Fine yellow plates of (IV e) (from glacial acetic acid) with m. p. 274° were formed.

Found %: N 6.72

$C_{39}H_{23}O_6N_3$. Calculated %: N 6.67

Reduction. A solution of 2 g of ethylamide (IV b) in 60 ml of glacial acetic acid was boiled with zinc dust until the solution was decolorized and then the mixture was diluted with water and treated with excess concentrated ammonia. This yielded 1.85 g of colorless ethylamide of 8-[di-o-benzylenolpyridyl-4^1]-1-naphthoic acid (VII) with m. p. 316-318° (from glacial acetic acid or xylene).

Found %: N 5.91

$C_{32}H_{24}O_3N_2$. Calculated %: N 5.78

Diethylamide of 8-[2^1, 3^1 (CO), 6^1, 5^1 (CO)-dibenzoylenepyridyl-4^1]-1-naphthoic acid (IV c). A mixture of 1.8 g of the acid chloride of acid III, 150 ml of dry chloroform, and 10 ml of diethylamine was boiled on a water bath for 2 hr, the bulk of the chloroform removed, and alcohol and water were added. The precipitate was purified by treatment with 0.5% NaOH. This yielded a yellow substance with m. p. 332° (from glacial acetic acid). It was insoluble in alcoholic alkali and did not change color.

Found %: N 5.55

$C_{34}H_{24}O_3N_2$. Calculated %: N 5.51

The spectra were plotted on a SF-4 spectrophotometer. The authors would like to thank A. Grinvald for plotting the spectra.

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EFFECT OF ADDED POTASH AND PHOSPHORIC ACID ON THE AROMATIZING ACTIVITY OF CHROMIUM OXIDE

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In our previous work [1] it was shown that alkali and alkaline earth elements have a promoting action on the aromatizing activity of an aluminochromium catalyst in dehydrocyclization of n-heptane and dehydrogenation of cyclohexane. Since the active principle of the two-component aluminochromium catalyst is chromium oxide, it seemed interesting to study the action of additives on the catalytic activity of pure chromium oxide in the conversions of hydrocarbons, the more so as Rubinshtein, Pribytkova, and Slinkin [2] observed that adding potassium to pure chromium oxide has an inhibiting effect in the dehydration and dehydrogenation of isopropyl alcohol.

Experiments at 450° and a space velocity of 0.8 hr^{-1} showed that the addition of potash (0.25 weight % of K_2O) completely suppresses dehydrocyclization of n-heptane, reduces the formation of unsaturateds by a factor of 7, and almost completely stops the secondary cracking and isomerizing action of the catalyst. This additive had the same effect on the dehydrogenation of cyclohexane to benzene, completely suppressing the reaction. However, when a mixture of n-heptane and n-1-heptene was passed over a catalyst to which potash had been added, toluene was formed; the yield of it was only a factor of 2.5 less than the yield of toluene from the same mixture passed over pure chromium oxide catalyst under the same conditions.

In order to determine whether the inhibiting action of potash was a specific effect of its alkaline nature, we studied the effect of added phosphoric acid (0.14 weight %) on chromium oxide under the same conditions. It was found to be identical with the effect of potash. The introduction of phosphoric acid suppressed dehydrocyclization of heptane, and dehydrogenation of cyclohexane to benzene and reduced the formation of toluene from a heptane-heptene mixture by a factor of approximately two. The introduction of both additives also decreased the hydrogenating power of the catalyst.

The experiments described led to the conclusion that the promoting action of the alkali element potassium on aluminochromium catalyst in the hydrocarbon reactions described cannot be ascribed solely to the reaction of the alkaline additive with the chromium oxide, but is more complex and apparently results from the interaction of all the three components, chromium oxide, aluminum oxide, and the alkaline additive, one form of which has been described in the work cited [2]. The fact that heptane and cyclohexane are not aromatized on pure chromium oxide after the introduction of potash or phosphoric acid while heptene is aromatized may be explained by the fact that the additives used in the present work affect the first stage of catalysis, namely, activated adsorption. It may be considered that the additives prevent the adsorption of saturated hydrocarbons on the active centers of the chromium catalyst, but have a much smaller effect on the adsorption of the more active olefin molecules.

The elucidation of the details of this phenomenon requires further investigation.

Experimental

The apparatus and procedures for the experiments and analyzing the catalyzate were the same as in the work cited above [1]. In experiments with a heptane-heptene mixture, the aromatic hydrocarbon content of the catalyzates was determined dispersiometrically due to the high concentration of unsaturated compounds. The catalyzates from all experiments were analyzed by gas – liquid chromatography. Two samples of pure chromium oxide were synthesized from analytical grade chromium nitrate. After final washing and drying in a drying cupboard, the samples were heated to 535° in a stream of air, cooled, and sieved.

For the experiments we used 5.5 ml portions (8.1 g, grain diameter 0.5-1.0 mm) of each sample. For the stabilization of fresh catalyst, it was used for aromatization of heptane at 535° for 2 hr and then regenerated. In order to decrease side reactions, the other experiments were carried out at 450° and a space velocity of 0.8 hr^{-1}. Before an experiment, the catalyst was heated to 535° in a stream of hydrogen and kept at this temperature for an hour for reduction of hexavalent to trivalent chromium. The catalyst was then cooled to 450° with the hydrogen still flowing, the hydrogen displaced with nitrogen from a tank for 3-4 min, and the experiment carried out. At the end of the experiment, the catalyst was flushed with nitrogen and regenerated with air; the regeneration time equalled the experiment time. The order of the experiments was as follows: first experiments with heptane, then with cyclohexane, and finally with heptane-heptene mixture.

After this, the regenerated first sample of catalyst was unloaded from the tube and impregnated with potash solution in an amount such that the potassium content of the catalyst corresponded to 0.25 weight % of K_2O. The catalyst was dried in a drying cupboard, stabilized by a 1-hr experiment with heptane at 535°, and then used for the other experiments in the same order as with the pure chromium oxide sample. A second sample of catalyst was impregnated with H_3PO_4 solution. The amount of phosphoric acid was in stoichiometric ratio to the potash and corresponded to 0.14 weight % of H_3PO_4 in the catalyst.

The starting heptane and cyclohexane were obtained by purification of commercial preparations [1]. 1-Heptene was synthesized by pyrolysis of 1-heptyl acetate and distilled twice on a column with an efficiency of 40 theoretical plates. The starting hydrocarbons had the following constants:

	B.p., °C/760 mm	n_D^{20}	d_4^{20}
n-Heptane	98,4	1,3878	0,6837
Cyclohexane	80,7	1,4256	0,7786
n-Heptene-1	93,6	1,3995	0,697

As we had a comparatively small amount of heptene, we carried out the experiments with a heptane-heptene mixture with the following constants: n^{20}_D 1.3928; d^{20}_4 0.690. The bromine number was 78.2. The mixture contained 46 weight % of heptene according to preparation and 48% according to bromine number.

Preliminary experiments at 535° showed that the pure chromium oxide we prepared was poisoned during aromatization at this temperature. Table 1 gives experiments at 450° with both pure chromium oxide and chromium oxide with additives. The mean yield of catalyzate in experiments with heptane was 88% and somewhat lower (84%) in experiments with mixture.

The introduction of potassium into pure chromium oxide completely suppressed the aromatization of heptane and there was no peak corresponding to toluene on the chromatogram of the catalyzate from experiment 3. Chromatography of the catalyzate from experiment 4, in which phosphoric acid was added to the catalyst, showed the presence of traces of toluene. It is possible that this difference is explained by the high activity of the second sample of pure chromium oxide as is shown by the results of experiments 1 and 2.

The yield of unsaturated hydrocarbons from heptane decreased from 11 to 1.6% on addition of potassium and from 13 to 3% on addition of phosphoric acid. A considerable portion of the unsaturated hydrocarbons obtained on catalysts with additives evidently consisted of cracking products. Unfortunately, we were unable to determine the 1-heptene content of the catalyzates. It was found that n-heptane and 1-heptene were not separated by gas-liquid chromatography with dionyl phthalate as the stationary phase.

TABLE 1

Aromatization on Chromium Catalysts

Experiment No.	Substance	Sample No. and substance added to Cr_2O_3	Amount passed, ml	Yield in weight % on hydrocarbon passed	
				aromatic	unsaturated
1	Heptane	№ 1 without addi-	12,5	10	10,8
2	»	№ 2 » » tive	13,3	14	12,5
3	»	№ 1+0,25% K_2O	13,3	0	1,6
4	»	№ 2+0,14% H_3PO_4	8,4	1	3,4
5	Cyclohexane	№ 1 w'out additive	11,1	52	1,6
6	»	№ 2 » »	8,9	51	1,1
7	»	№ 1+0,25% K_2O	8,5	0	0,3
8	»	№ 2+0,14% H_3PO_4	10,4	1	1,5
9	Mixt $C_7H_{16}+C_7H_{14}$	№ 1 w'out additive	8,9	17	19,9
10	The same	№ 1+0,25% K_2O	8,9	6	34,5
11	» »	№ 2+0,14% H_3PO_4	8,5	8	41,0

The aromatization of cyclohexane also ceased after potash and phosphoric acid had been introduced into the chromium catalyst. It is possible that in the experiments with cyclohexane, the unsaturateds were mainly products from slight cracking. The introduction of potassium decreased their yield from 1.6 to 0.3% (catalyst sample 1), while the introduction of phosphoric acid increased the yield of unsaturateds from 1.1 to 1.5% (sample 2).

In the aromatization of heptane-heptene mixture on pure chromium oxide, the yield of aromatics was 17 weight % on the mixture or 35% on the heptene passed. The additives reduced the yield of aromatics by a factor of approximately 2.5. It should be noted that the total yield of unsaturateds and aromatics during the aromatization of the mixture on pure chromium oxide (experiment 9) was less than the heptene content of the original mixture. This was apparently caused by the fact that during the aromatization, there was hydrogenation of part of the heptene by hydrogen liberated during dehydrocyclization. In experiment 10 (addition of potash), the total of unsaturateds and aromatics was 41%, i.e., there was hardly any hydrogenation of heptene when potassium was added to pure chromium oxide. In experiment 11 the total yield of these hydrocarbons was 49%; in other words, within the limits of experimental error, the hydrogenation of heptene practically ceased when phosphoric acid was introduced. Comparison of chromatograms showed that the introduction of potassium sharply reduced the yield of cracking and isomerization products of heptene. On the other hand, the introduction of phosphoric acid slightly increased cracking and, as might have been expected, increased isomerization of heptene.

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SLOW DISSOCIATION OF ASSOCIATES OF ALKOXYL AND ALKYL DERIVATIVES OF METALS IN SOLUTIONS

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In previous communications [1, 2] we reported a phenomenon which we observed, namely, slow decomposition of associates of alkoxyl derivatives of titanium in dilute benzene solutions (at constant solution concentration and constant temperature).

We have now established that this phenomenon occurs in solutions of organic compounds of other classes. It was found that the degree of association in solution of alkoxyl derivatives of tin, zirconium, and aluminum, as shown by cryoscopic determinations, falls with time and reaches unity after several hours.

Figure 1 gives curves of the change with time in the molecular weight of $(n\text{-}C_3H_7O)_4Sn$ in benzene solution at a concentration of 0.100 mol. % (curve 1) and the analogous curve for $(n\text{-}C_4H_9O)_4Zr$ (concentration of benzene solution 0.161 mol. %) (curve 2).

Tetra-n-propoxytin was obtained by the reaction of stannic chloride with n-propanol in the presence of ammonia [3]. The product was recrystallized from a mixture of hexane and benzene.

	Found %:	C 39.73; 39.65;	H 7.69; 7.74
$Sn(OC_3H_7)_4$.	Calculated %:	C 40.59;	H 7.95

Tetra-n-propoxytin is a waxy mass, which decomposes [4] during vacuum distillation at 0.03 mm. Tetra-n-butoxyzirconium was obtained [5] by the action of n-butanol on zirconium tetraacetylacetonate. The product was purified by distillation at $1.5 \cdot 10^{-3}$ mm.

	Found %:	C 49.81; 49.80;	H 9.36; 9.29;	Zr 23.91; 23.60
$(C_4H_9O)_4Zr$.	Calculated %:	C 49.65;	H 9.46;	Zr 23.79 *

Figure 2 gives curves showing the change in molecular weight of $(iso\text{-}C_4H_9)_2AlOC_2H_5$ in benzene solution with a concentration of 0.099 mol. % with time (curve 1) and analogous curves for $(n\text{-}C_3H_7O)_3Al$ (benzene solution concentration 0.112 mol. %, curve 2) and for $(iso\text{-}C_4H_9O)_3Al$ (benzene solution concentration 0.109 mol. %, curve 3).

Diisobutylethoxyaluminum was obtained by the action of ethanol on triisobutylaluminum [6].

	Found %:	C 64.40; 64.49;	H 12.40; 12.39;	Al 14.42; 14.69
$(C_4H_9)_2AlOC_2H_5$.	Calculated %:	C 64.48;	H 12.45;	Al 14.48

B.p. 125-126° at 2 mm. Literature data [7]: b.p. 110-114° at 1 mm.

*R. Kh. Freidlina and E. M. Brainina kindly supplied us with a sample.

Tri-n-propoxyaluminum was obtained by the action of aluminum on n-propanol.

Found %: Al 13.30; 13.63

$(C_3H_7O)_3Al$. Calculated %: Al 13.21

M.p. 105-106°. Literature data [8]: m. p. 106°.

Triisobutylaluminum was obtained by the action of aluminum on isobutanol.

Found %: C 58.05; 58.08; H 10.94; 11.02; Al 10.96; 11.35

$(C_4H_9O)_3Al$. Calculated %: C 58.51; H 11.05; Al 10.95

B.p. 247° at 12 mm. Literature data [8]: b.p. 250° at 12 mm.

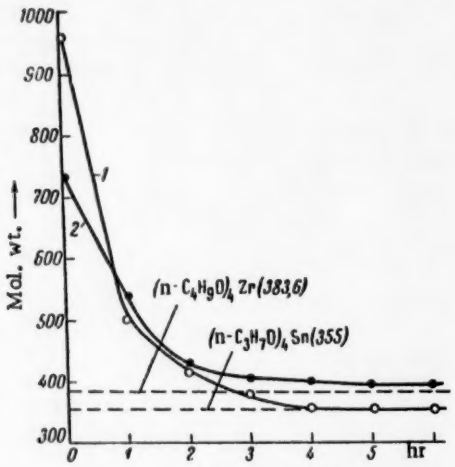

Fig. 1.

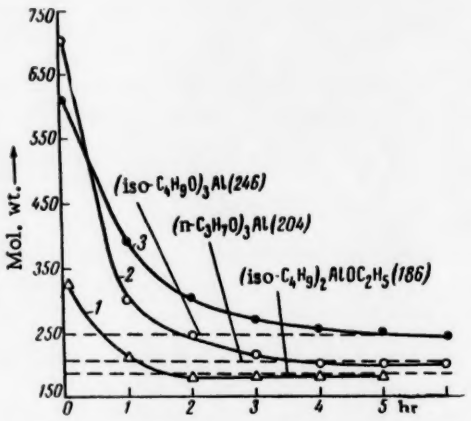

Fig. 2.

Trimethylaluminum is known to be dimeric [9-19] in vapor and solution. Triethylaluminum has also been shown to be dimeric in solutions [9, 15, 18, 19].

Molecules of trialkyl derivatives of gallium [18] and dialkyl derivatives of beryllium [18, 20] are dimeric. As has been established by a number of authors [11-14, 16], this dimerization is caused by the alkyl bridge, three-centered structure of these organometallic substances. It is therefore extremely interesting that slow decomposition of associates occurs not only in the case of alkoxyl derivatives of metals, but also with their alkyl derivatives, as we observed with alkyl derivatives of aluminum. In actual fact, the dimer of triethylaluminum slowly dissociates to the monomer stage in dilute benzene solutions at constant concentration and solution temperature.

Figure 3 shows a curve of the change with time in the molecular weight of $(C_2H_5)_3Al$ in benzene solution at a concentration of 0.100 mol. %.

The triethylaluminum was synthesized and its molecular weight determined in an atmosphere of pure dry argon. We obtained triethylaluminum by the action of ethyl bromide on aluminum and then symmetrization of the sesquibromide obtained by sodium [6].

Found %: C 63.56; 63.32; H 13.57; 13.33; Al 23.62; 23.46

$Al(C_2H_5)_3$. Calculated %: C 63.13; H 13.24; Al 23.63

B.p. 66-68°/0.5-1 mm.

According to our observations, associates formed through hydrogen bonds do not undergo slow dissociation in solutions. The molecular weight of acetic acid (corresponding to the dimer) in benzene solution at a concentration of 0.397 mol. % remained constant for many hours (23 hr). We observed the same in the case of phenol (benzene solution concentration 0.208 mol. %).

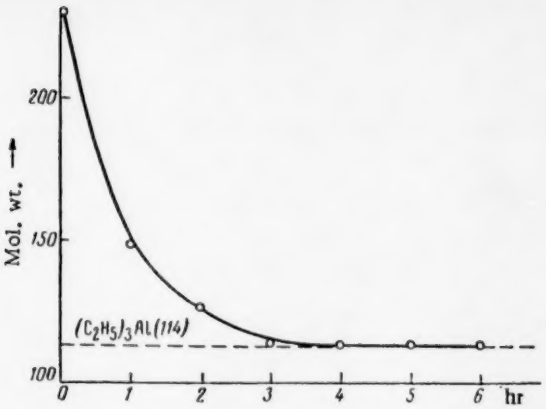

Fig. 3.

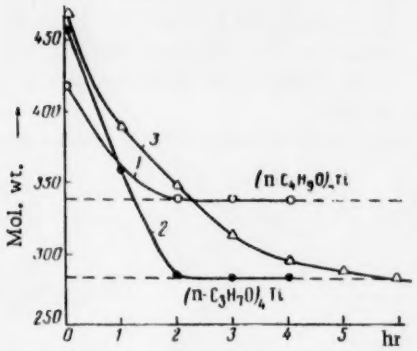

Fig. 4.

We also followed the dissociation of associated alkoxyl derivatives of titanium in oxygen-containing solvents, namely, dioxane and nitrobenzene, and also in cyclohexane. It was found that slow decomposition of associates may be observed in these solvents but, as was to be expected, dissociation in dioxane and nitrobenzene proceeded much more rapidly than in benzene.

In Fig. 4, curve 1 shows the change with time in the molecular weight of $(n\text{-}C_4H_9O)_4Ti$ in nitrobenzene (concentration 0.107 mol. %), curve 2 shows the change with time in the molecular weight of $(n\text{-}C_3H_7O)_4Ti$ in dioxane at a concentration of 0.254 mol. % (we used a dioxane solution of $(n\text{-}C_3H_7O)_4Ti$ at this concentration as at a concentration of 0.1 mol. %, which we usually used, tetrapropoxytitanium was not associated due to the "dioxane effect"), and curve 3 gives the change with time in the molecular weight of tetra-n-propoxytitanium in cyclohexane (concentration 0.105 mol. %).

Tetra-n-butoxytitanium was obtained by the reaction of n-butanol and titanium tetrachloride in the presence of ammonia [21]. It had b.p. 161-162° at 2 mm and n_D^{20} 1.4910. Literature data: b.p. 160-162° at 2 mm [22] and n_D^{20} 1.4910[23].

Tetra-n-propoxytitanium was obtained by the same method [21]. It had b.p. 138° at 1.5 mm and n_D^{20} 1.492. Literature data [23]: b.p. 135-136° at 1 mm and n_D^{20} 1.4979.

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2-PHENYL-4-HEXAFLUOROISOPROPYLIDENE-5-OXAZOLONE

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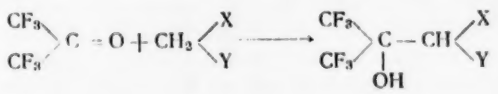
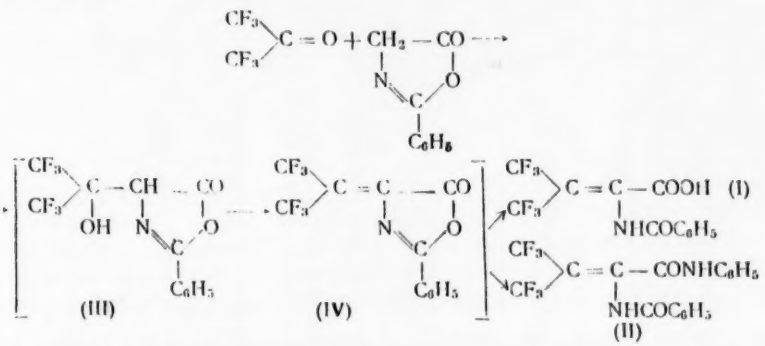
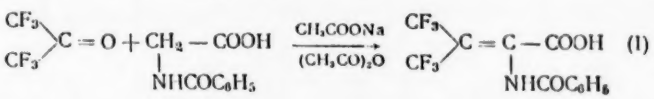
The reaction of hexafluoroacetone with compounds containing active methylene groups usually yields hydroxy compounds which do not undergo dehydration even under drastic conditions [1-3].



However, the reaction of hexafluoroacetone with 2-phenyl-5-oxazolone yielded α-benzamidohexafluorodimethylacrylic acid (I). If the reaction mixture was treated with excess aniline, the anilide of α-benzamidohexafluorodimethylacrylic acid (II) was obtained. The ease of dehydration of the intermediate hydroxyoxazolone (III) is evidently explained by the formation of the strongly conjugated system of 2-phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV):



α-Benzamidohexafluorodimethylacrylic acid (I) was also obtained under the conditions of the Erlenmeyer reaction [4] from hexafluoroacetone and hippuric acid:



By the action of ketene or acetic anhydride, acid I was readily converted into 2-phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV):

TABLE 1

Reaction of 2-Phenyl-4-hexafluoroisopropylidene-5-oxazolone with Nucleophilic Reagents

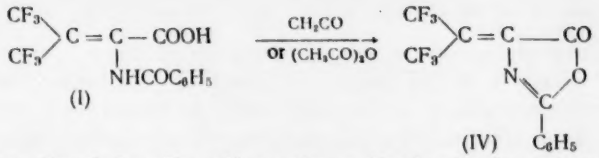
Nucleophilic compound	Reaction product	Solvent	Reaction time, hr	Yield, % of theoretical	B.p., °C	Found, %				Calculated, %			
						C	H	F	N	C	H	F	N
Water	α-Benzamidohexafluorodimethylacrylic acid* (I)	Ether	190	57	164—166 (decomp) (dichloroethane)	44,30 44,16	2,29 2,15	36,25 35,88	4,30	44,04	2,16	34,84	4,28
Methanol	Methyl ester of α-benzamidohexafluorodimethylacrylic acid** (V)	Benzene***	20	93,5	86—86,5 (hexane)	46,04 45,94	2,74 2,67	34,41 33,96	4,31 4,30	45,76	2,66	33,41	4,11
Ethanol	Ethyl ester of α-benzamidohexafluorodimethylacrylic acid (VI)	Benzene***	24	95	57—57,5 (hexane)	47,34 47,06	3,12 3,09	32,25 32,45		47,33	3,12	32,09	3,94
Ammonia	Amide of α-benzamidohexafluorodimethylacrylic acid (VII)	Ether	5	37	147—147,5 (benzene)	44,30 44,06	2,54 2,46	34,28 34,96	8,99 8,95	44,18	2,47	34,95	8,59
Ammonia****	Amide of α-amino-α-benzamidobis-(trifluoromethyl)-propionic acid* (XI)	Benzene	0,3	91,8	140—145 (decomp) (aqueous alcohol)	42,34 42,02	3,33 3,44	33,58 32,80	12,26 12,34	41,99	3,23	33,21	12,25
Aniline	Anilide of α-benzamidohexafluorodimethylacrylic acid* (II)	Benzene	0,1	60	215—215,5(decomp) (aqueous alcohol)	53,65	3,07	28,29	6,94	53,74	3,01	28,34	6,97
Benzylamine	Benzylamide of α-benzamidohexafluorodimethylacrylic acid (VIII)	Benzene	0,1	86	180—181 (alcohol)	54,67 54,66	3,32 3,42	28,97 28,71		54,81	3,39	27,38	6,73
Thiophenol	Thiophenyl ester of α-benzamidohexafluorodimethylacrylic acid* (IX)	Ether	2	47,6	115,5—117,5 (hexane)	51,89 52,18	2,75 2,74	27,96 26,41		51,54	2,64	27,18	3,34
Ethyl ester of glycine	Ethyl ester of N-(α-benzamidohexafluorodimethylacrylyl)-glycine (X)	Ether	24	77,3	133,5—135 (benzene)	46,34 46,24	3,31 3,32	27,49 27,53	6,61 6,72	46,61	3,42	27,65	6,80

* 2-Phenyl-4-isopropylidene-5-oxazolone does not react under the same conditions.

** V was also obtained by treatment of I with diazomethane in ether.

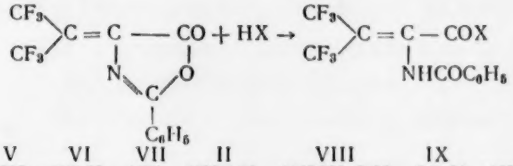
*** In the presence of catalytic amounts of triethylamine; the reaction was also carried out without catalyst in excess alcohol, but the product was obtained in lower yields.

**** Excess ammonia.



α-Benzamidohexafluorodimethylacrylic acid was also cyclized under the action of hexafluoroacetone.

2-Phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV) was found to be much more reactive than its unfluorinated analog, 2-phenyl-4-isopropylidene-5-oxazolone. Even at room temperature and without catalysts it reacted readily with nucleophilic compounds (water, alcohols, ammonia*, aniline, benzylamine, thiophenol, and the ethyl ester of glycine) to form the corresponding derivatives of α-benzamidohexafluorodimethylacrylic acid (I, II, and V-X).

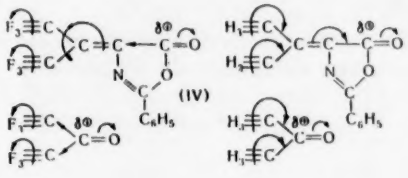


I V VI VII II VIII IX X

X = OH, OCH_3, OC_2H_5, NH_2, NHC_6H_5, $NHCH_2C_6H_5$, SC_6H_5, $NHCH_2COOC_2H_5$

The unfluorinated analog, 2-phenyl-4-isopropylidene-5-oxazolone, reacts with such compounds under much more drastic conditions, namely, with heating and in the presence of catalysts (acids and alkalis) [6-14].

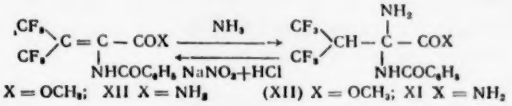
The ease with which 2-phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV) reacts with nucleophilic agents is probably explained by the fact that the presence of the electron acceptor trifluoromethyl groups decreases the electron density at the carbonyl carbon atom due to the combined action of the conjugation and induction effects, while in 2-phenyl-4-isopropylidene-5-oxazolone, the electron-donor methyl groups act in the opposite direction. The oxazolone IV may be regarded as the vinylog of hexafluoroacetone: the latter is known to react with nucleophilic compounds much more readily than acetone [1, 2].



Experimental

α-Benzamidohexafluorodimethylacrylic acid (I). With cooling in ice water, 38 g of hexafluoroacetone was passed into a solution of 18.8 g of 2-phenyl-5-oxazolone in 80 ml of pyridine. After the mixture had been kept at room temperature for 1 hr, it was poured into dilute hydrochloric acid with cooling. The oil was extracted with ether, the ether extract dried, and the ether and excess hexafluoroacetone hydrate removed by distillation. We obtained 21.69 g (56.8% of theoretical) of I; the m. p. and results of elementary analysis are given in Table 1.

* The amide of α-amino-α-benzamidobis-(trifluoromethyl)-propionic acid (XI) was obtained with excess ammonia. Ammonia also added readily to the methyl ester of α-benzamidohexafluorodimethylacrylic acid to form the methyl ester of α-amino-α-benzamidobis-(trifluoromethyl)-propionic acid (XII); it is interesting that these compounds reacted with nitrous acid, losing ammonia and changing into the original unsaturated compounds (V):



(V) X = OCH_3; XII X = NH_2 (XII) X = OCH_3; XI X = NH_2

See [3, 5] for the order of addition to an unsaturated system containing two trifluoromethyl groups.

The same acid was obtained from hexafluoroacetone and hippuric acid by heating the latter to 50-60° in acetic anhydride in the presence of sodium acetate.

Anilide of α-benzamidohexafluorodimethylacrylic acid (II). Into a solution of 0.52 g of α-benzamidohexafluorodimethylacrylic acid (I) in 4 ml of pyridine was passed 2.8 g of hexafluoroacetone. With cooling, 2 ml of aniline was added and the mixture kept at room temperature for 20 min and then poured into dilute hydrochloric acid; the solid substance obtained was recrystallized from aqueous alcohol. The yield was 0.11 g (17.4% of theoretical); the m. p. and results of elementary analysis are given in Table 1.

II was also obtained by the reaction of aniline with a pyridine solution of 2-phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV), obtained from hexafluoroacetone and 2-phenyl-5-oxazolone (see preparation of I).

2-Phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV). Excess ketene (about 7 g) was passed into a solution of 7.0 g of α-benzamidohexafluorodimethylacrylic acid (I) in 30 ml of absolute ether over a period of 30 min. Removal of the solvent yielded 6.1 g (92% of theoretical) of IV with m. p. 82-84° (from hexane).

Found %:	C 46.43;	H 1.60;	F 36.37;	N 4.53
$C_{12}H_5F_6O_2N$. Calculated %:	C 46.61;	H 1.63;	F 36.87;	N 4.53

IV was also obtained by heating acid I with acetic anhydride on a boiling water bath.

Reaction of 2-phenyl-4-hexafluoroisopropylidene-5-oxazolone (IV) with nucleophilic reagents. All the reagents tested were allowed to react with 2-phenyl-4-hexafluoroisopropylidene-5-oxazolone at room temperature without catalyst in ether or benzene; an equimolecular amount of the reagent was usually used (IV was hydrolyzed with water by shaking an ether solution of it with excess water).

The yields, melting points, and elementary analysis results for the products obtained are given in Table 1.

Methyl ester of α-amino-α-benzamidobis-(trifluoromethyl)-propionic acid (XII). Into a solution of 6.82 g of the methyl ester of α-benzamidohexafluorodimethylacrylic acid (V) in 50 ml of absolute ether was passed a large excess of gaseous ammonia at room temperature. Cooling the solution to −70° yielded 5.0 g (69.7% of theoretical) of XII with m. p. 99.5-103.5° (from hexane).

Found %:	C 43.10;	43.24;	H 3.33;	3.31;	F 31.23;	31.16;	N 7,83;	7.81
$C_{13}H_{12}F_6O_3N_2$. Calculated %:	C 43.58;		H 3.37;		F 31.82;		N 7.82;	

Treatment of a solution of XII in dilute hydrochloric acid with sodium nitrite yielded V with m. p. 84-86° (from hexane) and a mixed melting point with authentic V was not depressed.

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**See C.B. translation.

NEW REACTION OF TRIALKYLSILANES WITH ACID CHLORIDES OF ALIPHATIC MONOCARBOXYLIC ACIDS IN THE PRESENCE OF ALUMINUM CHLORIDE

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In the presence of $AlCl_3$, trialkylsilanes readily reduce alkyl halides to the corresponding hydrocarbons [1-3] and aromatic acid chlorides to aldehydes [4]. The reaction proceeds according to the general scheme:

$$R_3SiH + R'X \xrightarrow{AlCl_3} R_3SiX + R'H,$$

where R' is a hydrocarbon or acyl radical and X is a halogen.

It seemed interesting to study this reaction with acid chlorides of aliphatic monocarboxylic acids. For this purpose we studied the reduction of acetyl, n-butyryl, trimethylacetyl, and β-trimethylsilylpropionyl chlorides by triethylsilane. It was found that hardly any reaction of the reagents was observed in the absence of aluminum chloride. However, when catalytic amounts of $AlCl_3$ (2-3 mol. %) were introduced into a mixture of triethylsilane and acid chloride, there was immediate strong evolution of heat. The spontaneous boiling of the reaction mixture was then maintained by gentle heating and continued for about 4 hr.

TABLE 1

Products from the Reaction of Triethylsilane with Acid Chlorides of Aliphatic Monocarboxylic Acids in the Presence of 2-3 mol. % of $AlCl_3$

Starting RCOCl	Reaction products: $RCOOCH_2R$*							$(C_2H_5)_3SiCl$**
	compound	b.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Yield %	Yield %
CH_3COCl	$CH_3COOC_2H_5$	a) 76—79 (759)	0.8990	1.3727	22,34	22,28	54,2	66,3
$n\text{-}C_3H_7COCl$	$C_2H_5COOCH_2C_2H_7$	b) 164—165 (762)	0.8719	1.4073	40,66	40,78	60,0	91,6
$(CH_3)_3CCOCl$	$(CH_3)_3CCOOCH_2C_2(CH_3)_3$	c) 162—165 (761,5)	0.8431	1.4060	50,20	50,29	31,4	78,5
$(CH_3)_2SiCH_2-CH_2COCl$	$(CH_3)_2SiCH_2CH_2COO-CH_2CH_2CH_2Si(CH_3)_3$	143—144 (21)	0.8684	1.4368	78,56	78,72	54,6	76,3

* Literature data for esters: a) b.p. 77.15°; $n^{20}D$ 1.37239; d^{20}_4 0.90063 [5]; b) b.p. 166.25°; $n^{15}D$ 1.4087; d^{15}_4 0.8712 [6]; c) b.p. 162-164° [7].

** In all cases, the triethylchlorosilane obtained had b.p. 143-147°; $n^{20}D$ 1.4309 [10]; d^{20}_4 0.8932. Literature data [8]: b.p. 146.5°; $n^{20}D$ 1.4313; d^{20}_4 0.8968.

Contrary to expectation and contrary to the data of Jenkins and Post [4], we did not observe the formation of the corresponding aldehydes, despite the fact that from 66 to 92% of the starting triethylsilane was converted to triethylchlorosilane. The reduction products of the acid chlorides, which we isolated in good yields, were the corresponding esters. The results of the experiments and the properties of the substances formed are given in Table 1.

The results obtained showed that we had discovered a new catalytic reaction between trialkylsilanes and acid chlorides of aliphatic monocarboxylic acids according to the following equation:

$$2R_3SiH + 2R'COCl \xrightarrow{AlCl_3} 2R_3SiCl + R'COOCH_2R',$$

where R = C_2H_5, R' = CH_3, n-C_3H_7, $(CH_3)_3C$, $(CH_3)_3SiCH_2CH_2$.

The mechanism of this reaction has not been established conclusively. Apparently there is intermediate reduction of the acid chloride by triethylsilane to the corresponding aldehyde, which then reacts with excess acid chloride according to the scheme:

$$R_3SiH + R'COCl \rightarrow R'CHO + R_3SiCl,$$

$$R'CHO + R'COCl \rightarrow R'COOCHClR'^{*},$$

$$R'COOCHClR' + R_3SiH \rightarrow R'COOCH_2R' + R_3SiCl.$$

However, we cannot exclude the possibility of direct ester condensation of the aldehydes formed.

Experimental

Starting materials. n-Butyryl (I), trimethylacetyl (II), and β-trimethylsilylpropionyl chlorides (III) were obtained by the action of thionyl chloride on the corresponding acids and had the following constants: I—b. p. 101.0 – 101.5°, n^{20}_D 1.4120; II—b. p. 103 – 106°; III—b. p. 70 – 71° (25 mm), n^{20}_D 1.4381.

Acetyl chloride was a commercial preparation and had b.p. 51-52.5°. Triethylsilane, which was prepared by organomagnesium synthesis, had b.p. 107-109°, $n^{20}D$ 1.4120. The aluminum chloride was a commercial "purified" preparation.

Reaction of triethylsilane with acetyl chloride. In a round-bottomed flask with a reflux condenser with a ground glass joint and a dropping funnel were placed 23.6 g (0.3 mole) of acetyl chloride and 0.8 g of aluminum chloride. Slight evolution of heat was observed. Then 34.9 g (0.3 mole) of triethylsilane was added over a period of 30-40 min. The reaction mixture evolved heat strongly and boiled spontaneously. Boiling was maintained by gentle heating for four hours and then the reaction mixture was distilled on an efficient fractionating column.

Distillation yielded 7.15 g (54.6%) of ethyl acetate with b. p. 76 – 79° (759 mm); n^{20}_D 1.3737; d^{20}_4 0.8990 and 30 g (66.3%) of triethylchlorosilane with b. p. 143 – 145°; n^{20}_D 1.4309.

Reaction of triethylsilane with butyryl chloride. Over a period of one and a half hours, 70 g (0.6 mole) of triethylsilane was added to a mixture of 64 g (0.6 mole) of butyryl chloride and 1.64 g of aluminum chloride. There was also evolution of heat by the reaction mixture, which was then boiled for four hours.

Distillation yielded 24.2 g (60.0%) of butyryl butyrate with b.p. 164-165° (762 mm); $n^{20}D$ 1.4073; d^{20}_4 0.8719 and 83.1 g (91.6%) of triethylchlorosilane with b.p. 143-147° (762 mm), $n^{20}D$ 1.4310.

Reaction of triethylsilane with trimethylacetyl chloride. When 1.2 g of aluminum chloride was added to 36.15 g (0.3 mole) of trimethylacetyl chloride there was vigorous gas evolution accompanied by a sharp fall in the temperature of the reaction mixture. Gas evolution ceased immediately when 34.8 g (0.3 mole) of triethylsilane was added. The subsequent procedure was as in the previous experiment.

Distillation yielded 16.2 g (31.4%) of β-trimethylethyl trimethylacetate with b. p. 162 – 165.5° (761.5 mm); n^{20}_D 1.4160; d^{20}_4 0.8431 and 35.4 g (78.5%) of triethylchlorosilane with b. p. 143 – 147°, n^{20}_D 1.4309.

The ester was hydrolyzed by Schaefer's method by boiling for 6 hr with a 1 N ethylene glycol solution of potassium hydroxide. Titration was carried out with a double indicator (neutralization to thymolphthalein and titration of the potassium salt to bromophenol blue).

Ester number found 324.1; 324.5; Molecular weight (cryoscopically in benzene), found: 173.1; 171.1, $C_{10}H_{20}O_2$ calculated: 172.28.

* The condensation of aldehydes with acid chlorides according to the scheme given has been described in the literature [9].

Reaction of triethylsilane with β-trimethylsilylpropionyl chloride. To a mixture of 50 g (0.3 mole) of β-trimethylsilylpropionyl chloride and 1.2 g of aluminum chloride was added 46.5 g (0.4 mole) of triethylsilane. The mixture evolved heat strongly. The mixture was kept boiling for four hours.

Distillation yielded 21.6 g (54.6%) of γ-trimethylsilylpropyl β-trimethylsilylpropionate with b. p. 143–141° (21 mm); $n^{20}D$ 1.4368; d^{20}_4 0.8634 and 46 g (76.3%) of triethylchlorosilane with b. p. 143–146°; $n^{20}D$ 1.4308; d^{20}_4 0.8932.

The ester was hydrolyzed as in the previous experiment. Ester number found: 212.8; 213; calculated 215. Molecular weight (cryoscopically in benzene) found: 255.8; 265.4; $C_{12}H_{28}Si_2O_2$, calculated 260.48.

Found %:	Si 21.21;	21.53;	C 55.81;	55.76;	H 11.28;	11.69
Calculated %:	Si 21.68;		C 55.23;		H 10.83	

Experiments with a change in the order of addition of the reagents (acid chloride was added to a mixture of triethylsilane and aluminum chloride) gave analogous results.

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SPECTROPHOTOMETRIC STUDY OF CHLORIDE COMPLEXES OF COBALT IN MELTS

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The study of the state of ions in melts is of great theoretical and practical value as molten salts form the most common class of inorganic solvents. Spectrophotometry is the classical method of studying aqueous and non-aqueous solutions and it must be assumed that the application of this method to the molten state leads to no less valuable results. Practical work in this direction is only just beginning [1-5]. However, spectrophotometry has not been used with physicochemical analysis procedures and therefore the value of data of the corresponding measurements is, to a certain extent, limited.

The present work was devoted to the study of chloride complexes of Co^{2+} in a $LiNO_3-KNO_3$ melt of approximately eutectic composition.

The measurements were carried out on an SF-4 spectrophotometer with a specially fitted cell compartment, consisting of a massive block of stainless steel (Fig. 1), five faces of which were surrounded by a heater spiral. A number of openings were cut in the block: two round vertical ones for a thermometer or thermocouple, a square vertical one for the cell-holder, and two horizontal through holes in perpendicular planes (for the light beam measured and for introducing a device for changing the position of the cell in the light beam). On top of the block was fixed a thermally insulated lid of stainless steel. The sides and bottom were thermally insulated with chamotte brick. The block was placed in a welded steel casing between whose double walls flowed thermostatted water. The casing was covered with a steel lid with double walls. The walls and lid of the casing had holes for passage of the light beam, movement of the cell-holder, the introduction of thermometers or thermocouples, and filling the block with an inert gas. The cell compartment was firmly fixed to a special support between the light source and the body of the spectrophotometer. With this arrangement of the cell compartment, any radiation, including thermal radiation of the furnace, passed through the monochromator. The electric supply to the furnace block passed through a voltage stabilizer and a constant temperature was maintained visually with an accuracy of $\pm 1°$ C. The maximum working temperature was 900°. For the work we used standard 10-ml quartz cells.

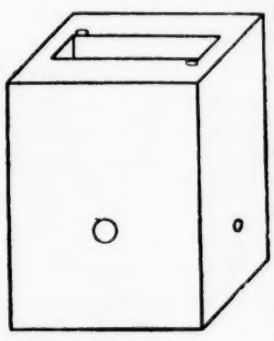

Fig. 1. Furnace block of spectrophotometer cell compartment.

All the reagents used were purified by two recrystallizations as even chemically pure substances were found to be insufficiently transparent on fusion.

The solvent was an anhydrous mixture of 45 mol. % of $LiNO_3$ and 55 mol. % of KNO_3. The solvent was dried with a stream of dry nitrogen passed through the melt at 220° for 4 hr. Co^{2+} and Cl^- ions were introduced into the system as $Co(NO_3)_2 \cdot 6H_2O$ and KCl. Preliminary experiments showed that the absorption spectrum of $Co(NO_3)_2$ and even its chloride complexes were not affected by small amounts of water and nitric acid present in the melt. Thus, the introduction into the melt at 160° of up to 3% of water (by volume) led only to an effect associated with dilution of the solution. In all experiments, the comparison cell contained solvent with the same amount of KCl as in the working solution. Measurements were made at 160, 200 and 240°. The

experimental data are given in Figs. 2, 3, and 4.

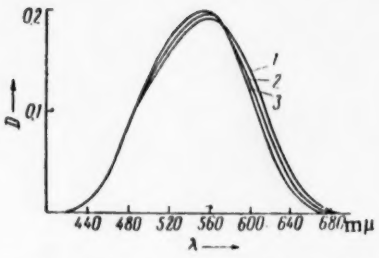

Fig. 2. Absorption spectrum of 0.0248 M solution of $Co(NO_3)_2$ in nitrate melt: 1) 240°; 2) 200°; 3) 160°.

As Fig. 2 shows, the absorption spectrum of a 0.0248 M solution of $Co(NO_3)_2$ depends little on temperature. There was only a slight displacement of the absorption maximum toward the long-wave region connected with weakening of the field of the ligands of the absorbing ion and a slight broadening of the absorption band caused by superposition of vibration transitions. The partial reduction in the absorption intensity at the band maximum may be associated to a considerable extent with thermal dilution of the solution. At the present time, many examples of splitting of the energy levels of the $3d^7$ configuration of the Co^{2+} ion in fields of different symmetry are being analyzed [6-10]. A comparison of the absorption bands with the nature of absorption bands of different octahedral complexes of cobalt, which is given in Fig. 2, indicates octahedral coordination of cobalt ions in the nitrate melt.

The displacement toward the long-wave region indicates weakening of the field of the ligands of the octahedral nitrate complexes in comparison with the fields of such ligands as NH_3, H_2O, and MgO and similar to the field strength of such ligands as F^- and the oxygen of sulfuric and phosphoric acids.

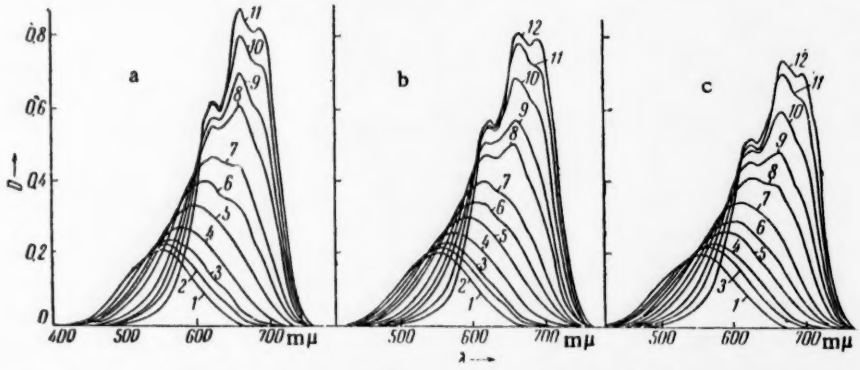

Fig. 3. Effect of complex formation on the absorption spectrum of 0.00248 M solution of $Co(NO_3)_2$ in nitrate melt. a) 160°; b) 200°; c) 240°. Molar ratios of KCl: $Co(NO_3)_2$: 1) 0; 2) 8; 3) 16; 4) 32; 5) 56; 6) 81; 7) 114; 8) 183; 9) 251; 10) 387; 11) 653; 12) 1160.

Figure 3 shows the changes in the absorption spectrum of a 0.00248 M solution of cobalt nitrate associated with the formation of chloride complexes. As may be seen, an increase in the potassium chloride concentration produced a displacement of the main absorption band toward the long-wave region and the successive appearance of three new absorption maxima, corresponding to the formation of three forms of complex ion, respectively. On the basis of many investigations of complex chlorides of cobalt in aqueous and nonaqueous solutions and melts [5], it was assumed that the complex formed in these systems was $[CoCl_4]^{2-}$. Therefore, the appearance of the longer-wave maximum (690 mμ) may be associated with the formation of this ion. In actual fact, this maximum appears at the highest concentrations of KCl when the maximum at 625 mμ has begun to decrease and that at 665 mμ has developed considerably. It is also characteristic that the position of the maximum at 690 mμ depends little on the nature of the solvent and other characteristics of the system, which confirms the tetrahedral structure of the ion $[CoCl_4]^{2-}$ [10, 11]. The absorption band with the center of gravity at about 625 mμ was caused by one of the lower chloride complexes of cobalt. The application of the method of Bodlander and Abegg [12] in the region of 660 mμ at KCl concentrations at which one might expect only the formation of complex particles giving absorption with a maximum at 625 mμ showed that the molecular compound $CoCl_2$ is formed under these

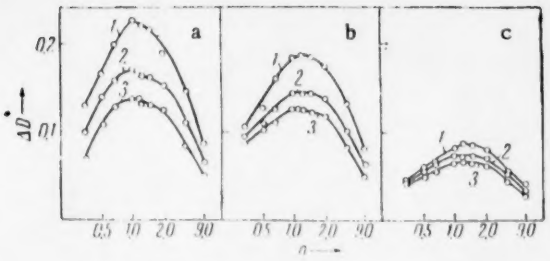

Fig. 4. Light absorption in the isomolar (0.0248 mole/liter) series of the system $Co(NO_3)_2-K_2Cl_2$: a) 600 mμ; b) 630 mμ; c) 660 mμ. Temperature: 1) 160°; 2) 200°; 3) 240°.

conditions. Thus, the maximum at 625 mμ is associated with the existence of particles of $CoCl_2$ and the maximum at 665 mμ is caused by absorbing centers with the composition $[CoCl_3]^-$. The dissociation constant of the molecular compound was estimated by means of this method. K_2 was of the order of $2 \cdot 10^{-2}$. It was not worth while to determine the temperature dependence of the instability constant of the complex as the absorption bands of the different complex particles overlapped and absorption in the region of 660 mμ could not be assigned to one compound even at very low KCl concentrations. The general nature of the dissociation of chloride complexes of Co^{2+} with a rise in temperature is clearly shown by Fig. 3. As the position of the absorption maxima did not change substantially, the main fall in absorption with an increase in temperature could be ascribed to dissociation of the complexes. Thus, chloride complexes are formed exothermally in a nitrate melt, which agrees completely with ideas on the higher stability of chloride complexes as compared with nitrate complexes. Chloride complexes are formed in aqueous and organic solutions [13, 14] with absorption of heat and complex formation occurs mainly due to an increase in entropy.

Figure 4 gives data on an isomolar series in the system $Co(NO_3)_2-K_2Cl_2$ at a total concentration of 0.0248 M. The values $n = \frac{C_{K_2Cl_2}}{C_{Co(NO_3)_2}}$, where C is the concentration in moles per liter, are plotted along the abscissa axis. The differences between the optical density of the solution investigated and the calculated optical density, caused by absorption of cobalt ions, are plotted along the ordinate axis. All concentrations were calculated for 160° with the specific gravity of the melt taken as 1.94 g/cc [4]. Data on the isomolar series shows that the predominating compound formed in the system is $CoCl_2$ and n = 1. This appears most clearly at λ = 600 mμ.

With an increase in the wavelength there was a displacement of the maximum toward the formation of compounds with a higher coordination number. At λ = 660 mμ, the maximum was flat and spread over the region of n = 1-2, i. e., over the region of complex compounds with the composition $CoCl_2-[CoCl_4]^{2-}$. Thus, the data on the isomolar series confirm the conclusions drawn previously. Attention is attracted by the over-all increase in ΔD in the case of data referring to λ = 600 mμ in comparison with analogous values at λ = 630 mμ. This evidently may be explained by the superposition of the absorption of particles which disappear at high concentrations of KCl (Fig. 3). These particles obviously may be $CoCl^+$ ions.

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METHOD OF ISOLATING AROMATIC HYDROCARBONS FROM MIDDLE (KEROSENE) FRACTIONS OF PETROLEUMS

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With the development of reagent technology, the value of relatively high-boiling fractions of petroleum has increased. In this connection, there has recently been an increase in interest in the chemical composition of these fractions, both here and abroad [1-6]. Below we present the results of investigating the hydrocarbon composition of a petroleum fraction in which the aromatic hydrocarbons were separated chromatographically with two adsorbents.

The petroleum sample used in the present investigation was taken from the Romashkinsk deposit (Aktash area, Mikhailov level). The ligroin fractions boiling up to 175° were removed from the petroleum by distillation on a single-stage evaporation apparatus. The asphalt was then removed from the deligroined petroleum by the cold fractionation method [7]. The deligroined and deasphalted petroleum was distilled on a vacuum apparatus with collection of appropriate fractions. The characteristics of the fraction boiling at 175-300° are given below:

$n^{20}D$	d^{20}_4	Aniline point	Iodine number	Flash point °C	Solidification p., °C	Tars	Asphaltenes
1.4612	0.8254	68.3	6	76.5	−33	Traces	Traces

The asphalt-tar materials were removed completely from the fraction.

For studying the chemical composition of the fraction, we used various methods of isolating and determining types of petroleum hydrocarbons: chromatographic separation, treatment with carbamide (determination of normal paraffins), catalytic dehydrogenation (determination of hexamethylene structures), and the aniline method. However, chromatographic isolation and separation of aromatic hydrocarbons was used mainly.

It was found that good results were obtained by chromatography in two stages: isolation and preliminary separation of all the aromatic hydrocarbons was carried out first and then the aromatic hydrocarbons isolated were separated into types more precisely.

The aromatic hydrocarbons were isolated from the fraction by chromatography on silica gel with displacement by ethanol. Before use, the silica gel (ASM grade, grain size 90-180 mesh) was treated by the method of Musaev and Iskhanova [8]. Two chromatographic separations on silica gel yielded seven fractions of aromatic hydrocarbons with refractive indices from 1.49 to 1.55.

The sulfur compounds were removed from the fractions isolated by oxidation with 25% hydrogen peroxide solution in glacial acetic acid at 80° with subsequent removal of the sulfoxides formed by chromatography on silica gel (ASK grade). As was demonstrated with some individual hydrocarbons, aromatic hydrocarbons are

affected only to an insignificant extent during oxidation under the given conditions.

According to their physicochemical properties, the fractions of aromatic hydrocarbons freed from sulfur compounds were mixtures of monocyclic and bicyclic aromatic hydrocarbons with monocyclic hydrocarbons predominating in the first fractions (with some naphthene - paraffin hydrocarbons) and bicyclic hydrocarbons in the final fractions. The fractions of aromatic hydrocarbons isolated were then separated more efficiently by chromatography on alumina. The alumina (GU-MKhP grade, Dneprodzerzhinsk factory) had a grain size of 100-180 mesh; before use it was dried at 150°. The alumina had the following characteristics: the specific surface 197 m^2/g, pore volume 0.809 ml/g, mean pore radius 80 A, and predominating pore radius 42 A.

A two-meter column was used for the chromatographic separation. In each experiment we used 30 g of aromatic hydrocarbon fraction and 300 g of alumina; as desorbents we successively used isooctane (500 ml), benzene (200 ml), and isopropanol (400 ml).

As experiments on the separation of individual hydrocarbons showed, monocyclic hydrocarbons were quantitatively separated from bicyclic aromatic hydrocarbons under the conditions adopted. As an example Table 1 gives the results of separating tert-isobutyl-o-xylene and butylnaphthalene, and also tert-isobutyl-o-xylene and biphenyl. These experiments were carried out with 2.5 ml samples of the mixtures and the losses during the chromatographic separation were therefore 6-9%.

TABLE 1

Results of Chromatographic Separation of Artificial Hydrocarbon Mixtures

Experiment No.	Hydrocarbons present in mixture	Composition of mixture before separation			Characteristics of aromatic hydrocarbons isolated from mixture			
		hydrocarbon content, %	n_D^{20}		monocyclic		bicyclic	
			hydrocarbons	mixture	yield, %	n_D^{20}	yield, %	n_D^{20}
	Adsorbent – alumina							
1	Tert-isobutyl-o-xylene	77,58	1,5000	1,5168	76,37	1,5000	—	—
	Butylnaphthalene	22,42	1,5820		—	—	17,97	1,5820
2	Tert-isobutyl-o-xylene	84,33	1,5000	1,5169	77,94	1,4995	—	—
	Biphenyl	15,67	(m.p. 69°)		—	—	13,06	
	Adsorbent – silica gel							
3	Tert-isobutyl-o-xylene	79,82	1,5000	1,5205	14,29	1,4995	—	—
	Biphenyl	20,18	(m.p.69°)		—	—	14,30	

As follows from the data in Table 1, chromatographic separation under the same conditions but on silica gel gave much poorer results. A large number of intermediate fractions was formed in this case.

In the chromatographic separation of aromatic hydrocarbons isolated from the petroleum fraction with b. p. 175-300° on alumina under the conditions described above, the total amount of monocyclic aromatic hydrocarbons was (on the aromatic part after desulfurization) 77.93% (13.11% on the fraction with b. p. 175-300°) and the corresponding amounts of bicyclic aromatic hydrocarbons were 17.91 and 3.01%.

It is interesting to note that with alumina as adsorbent, we obtained about 4% of intermediate fractions ($n^{20}D$ 1.5120–1.5700), which apparently contained hydrocarbons of mixed structure, containing a polymethylene ring in addition to a benzene ring. The former was confirmed by experiments on the separation of mixtures of individual hydrocarbons consisting of aromatic hydrocarbons and cyclopentyltoluene, tetralin and indan.

The over-all hydrocarbon composition of the fraction with b. p. 175-300° from Romashkinsk petroleum may be represented in the following way (in percentages): monocyclic aromatic hydrocarbons 18.2, bicyclic

aromatic hydrocarbons 4.2, aromatic hydrocarbons of mixed structure 1, hexamethylene hydrocarbons 6.4, pentamethylene hydrocarbons 15.5, normal paraffins 17.5, isoparaffins 41.2.

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ELECTRONIC NATURE OF FLUORINE-CONTAINING SUBSTITUENTS

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The properties of organic compounds containing fluorine atoms as substituents have been studied thoroughly. The pK values of fluorine-substituted benzoic acids, anilines, and phenols, the ultraviolet absorption spectra, the dipole moments and nuclear magnetic resonance spectra, have been determined. The properties of trifluoromethyl derivatives of benzene have also been studied quite thoroughly. The physicochemical properties of aromatic compounds with other fluorine-containing substituents are completely unknown. We began a study of them by determining the pK_a values of the corresponding benzoic acids. Data on the strength of acids are very valuable for obtaining information on the electronic nature of substituents in the m- or p- positions with respect to the carboxyl groups.

The pK_a values of the acids were determined by measurement of the pH of half-neutralized solutions. An accurately weighed sample of a fluorine-substituted benzoic acid (to give a concentration of 0.01 M) was dissolved in alcohol, half neutralized with a carbonate-free titration solution of sodium hydroxide, and diluted with water to give a 50-50 mixture of alcohol and water (by volume). The pH was measured with an LP-5 tube potentiometer with a glass electrode at 25°. A saturated calomel electrode was used as the reference electrode. The accuracy of the pH measurements was 0.03. For checking the measurement procedure, we determined the pK_a values of some fluorine-free acids: p-bromo-, p-nitro-, and p-methoxybenzoic acids.

The data obtained agreed with literature data [1]. We previously synthesized and described the benzoic acids with fluorine-containing substituents which we used for determination of pK_a.

The results of determining the pK_a values are given in Table 1, which also gives known values of pK_a for substituted benzoic acids in 50% aqueous ethanol for comparison.

Hammett [2] found a quantitative relation between the nature of the substituent in the meta- or para-position to the reactive center and the reactivity of the side chain and expressed it through the following equation:

$$\lg \frac{k}{k_0} = \rho\sigma,$$

where k and k_0 are the rate constants (or equilibrium constants) of the substituted and unsubstituted aromatic compounds, respectively, σ is a constant of the substituent characterizing its electronic effect on the reaction center, and ρ is a constant characteristic of the given reaction. Starting from the dissociation constants of benzoic acids with fluorine-containing substituents found, we calculated the σ constants of these substituents.

For finding the constant ρ we chose 6 substituents with accurately determined σ constants and pK_a of the corresponding benzoic acids in 50% aqueous ethanol and also used the data for pK_a and $\sigma = 0$ of unsubstituted benzoic acids. For calculating ρ, we used only pK_a values of m-derivatives of benzoic acid, as para conjugation has a large effect on the value of the σ constant for p-substituted derivatives.

Substituent	m-Position			p-Position		
	pK_a	$k \cdot 10^{-4}$	σ_m	pK_a	$k \cdot 10^{-4}$	σ_p
CF_3SO_2*	4,54	28,8	0,79	4,17	67,6	1,03
$CF_2(CF_2)O$*				4,51	30,9	0,81
NO_2	4,66 (1)	21,9	0,710 (5)	4,54 (1)	28,8	0,778 (5)
CH_3SO_2	4,78 (6)	16,6	0,645 (5)	4,68 (6)	20,9	0,72 (5)
CN	4,85 (7)	14,1	0,598 (5)	4,70 (7)	20,0	0,66 (5)
CF_3	5,11 (8)	7,7	0,428 (5)	4,94 (8)	11,2	0,54 (5)
CF_3O*	5,19	6,5	0,36	5,26	5,5	0,32
$CF_2(O)O$*				5,20	6,3	0,36
CF_3S*	5,21	6,2	0,35	5,17	6,8	0,38
CH_3CO	5,21 (6)	6,2	0,376 (5)	5,10 (6)	7,9	0,502 (5)
Br	5,22 (1)	6,0	0,391 (5)	5,35 (1)	4,5	0,232 (5)
$CF_3-CH=CH$* H	5,75 (1)	1,8	0	5,40	4,0	0,23

*Substituents for which the pK_a values and σ-constants were determined for the first time in the present work.

By means of these data and the method described in the review of Jaffe [3], we calculated $\rho = 1.535$, and also the correlation coefficient r and the standard error s. Taft [4] recently came to the conclusion that for finding ρ, it is only possible to use those substituents whose σ constants agree with the data of Hammett [2] or the values of McDaniel and Brown [5] within the limits of $\pm$ 0.07 unit and with a standard error of no more than $\pm$ 0.03. The substituents we chose, H, m-Br, CH_3CO, CF_3, CN, SO_2CH_3, and NO_2, satisfy these conditions as when $\rho = 1.535$, $r = 0.998$ and $s = 0.03$. In the calculation of ρ, we used the values of the σ constants for the substituents H, SO_2CH_3, CN, and CF_3, obtained from the values of pK_a in 50% alcohol, and for the substituents NO_2, Br, and $COCH_3$, from the values of pK_a in water [5]. From the value of ρ found, we calculated the σ constants of the new substituents in the m- and p-positions. The cyclic groupings $O(CF_2)_4$ and $CF_2(O)_2$ were included in the p-series in analogy with the $CH_2(O)_2$ grouping, tetralin, and hydrindene [2, 3]. Table 1 includes the m-substituents which we used for the calculation of ρ, and the pK_a values and σ constants of the corresponding p-substituents are also given for comparison. All the substituents presented are electron acceptors or very weak electron donors. The dissociation constants of the given acids are greater than the dissociation constants of benzoic acid and the values of the σ constants are positive. As is known, electron-donor substituents show opposite effects.

As Table 1 shows, the strongest electron-acceptor group among known substituents in the benzene ring is the trifluoromethylsulfonyl group. p-Trifluoromethylsulfonylbenzoic acid is more than twice as strong as p-nitrobenzoic acid.

The relation between the σ constants and the log K of substituted benzoic acid in 50% aqueous ethanol is shown in Fig. 1. The inductive effect of the CF_3SO_2 group is greater than that of the nitro group as m-trifluoromethylsulfonylbenzoic acid is stronger than m-nitrobenzoic acid. Like nitrobenzene, phenyltrifluoromethylsulfone is nitrated only in the meta position.

The grouping $CF_2(CF_2)O$ is electronegative and equal in strength to the nitro group. The σ constants of the groups CF_3O, CF_3S, $CF_2(O)_2$ are very similar to those of halogen atoms, bromine and chlorine (for the latter $\sigma_m = 0.373$, $\sigma_p = 0.227$ [5]).

Like halogens, these groups are ortho-para directing in electrophilic substitution in the aromatic nucleus. The substituent $CF_3CH = CH-$ differs sharply from the CF_3 group in its effect on the benzene ring. Nitration of phenyltrifluoromethylethylene yielded about 50% of the p-isomer, while benzotrifluoride is nitrated only in the m-position. p-$CF_3CH=CH$-benzoic acid, is similar in strength to p-bromobenzoic acid and not to p-trifluoromethylbenzoic acid, of which it is the vinylene homolog. The σ constants of the substituents $CF_3-CH = CH-$ and the bromine atom are the same and a factor of 2.5 less than the σ constant of the trifluoromethyl group.

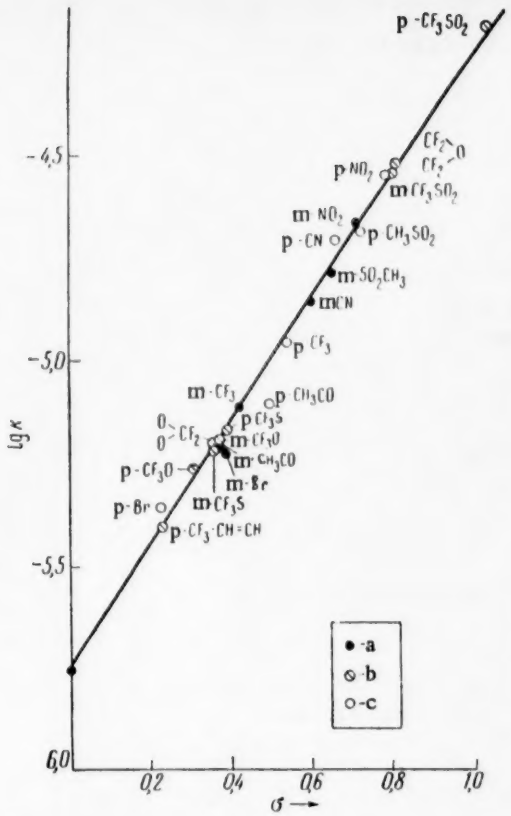

Fig. 1. a) Substituents from which ρ was calculated; b) substituents investigated in the present work; c) substituents given for comparison.

We also determined the pK_a in 50% aqueous ethanol of 2-trifluoromethyl-1-naphthoic acid (pK_a = 4.25; $k \cdot 10^{-6}$ = 56.2) and o-trifluoromethylbenzoic acid (pK = 4.69; $k \cdot 10^{-6}$ = 20.4). The former was found to be 2.5 times as strong an acid as the latter.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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Translated from Russian by Geoffrey D. Archard
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Devoted to a consideration of the mechanism and kinetics of crystallization and the production of single-crystal semiconductor materials, their purification and the controlled distribution of impurities. Several articles in this important new volume cover theoretical and experimental aspects of the relief and the state of the surface of growing crystals and the surface energy at crystal-melt boundaries. Attention is given to the competing mechanism in crystallization processes, compared with experimental data on the temperature-dependence of crystallization parameters, the linear velocity of crystallization, and the rate of crystal growth. A number of papers consider the structural and kinetic laws of crystal dissolution and the role of the structure of liquids in crystallization processes.

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